Atomic Structure

Learning Outcomes

- ☐ **Understanding of Atomic structure**- a) Ancient Model (Shell Model) b)Modern Structure
- ☐ **Discovery of three classical sub atomic particles-** Electron, Proton, Neutron
- ☐ Description of Thomson, Rutherford and Bohr's **atomic model.**
- ☐ Important Features of Quantum mechanical model.
- ☐ Nature of Electromagnetic Radiations and Planck's Quantum Theory
- ☐ Explanation of Photo electric Effect and Atomic Spectra
- ☐ Understanding of De- Broglie Equation, Heisenberg's Uncertainty Principle, Quantum number and atomic orbitals, Hund's Rule, Pauli's Exclusion Principle, Aufbau Rule
- ☐ Electronic Configuration of atoms (According to Aufbau Principle)

Introduction

ATOM

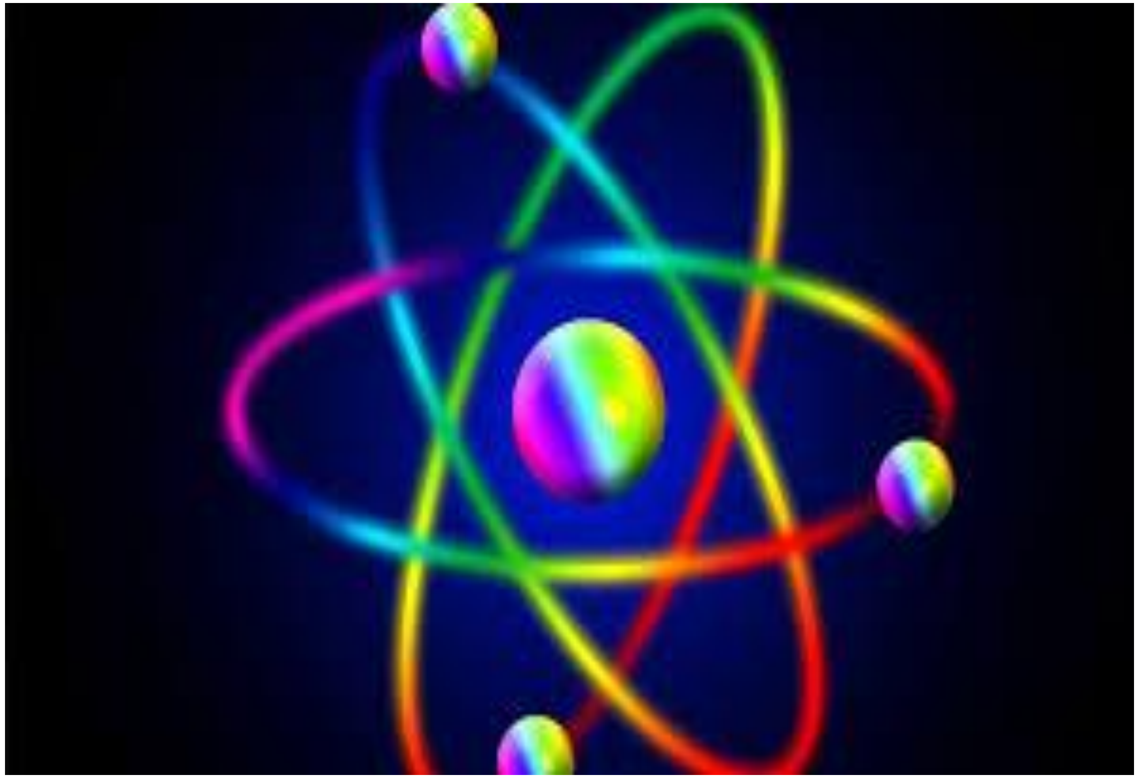
A means NOT

TOM (A Greek word) means Divisible

Let’s Have a Quick Look

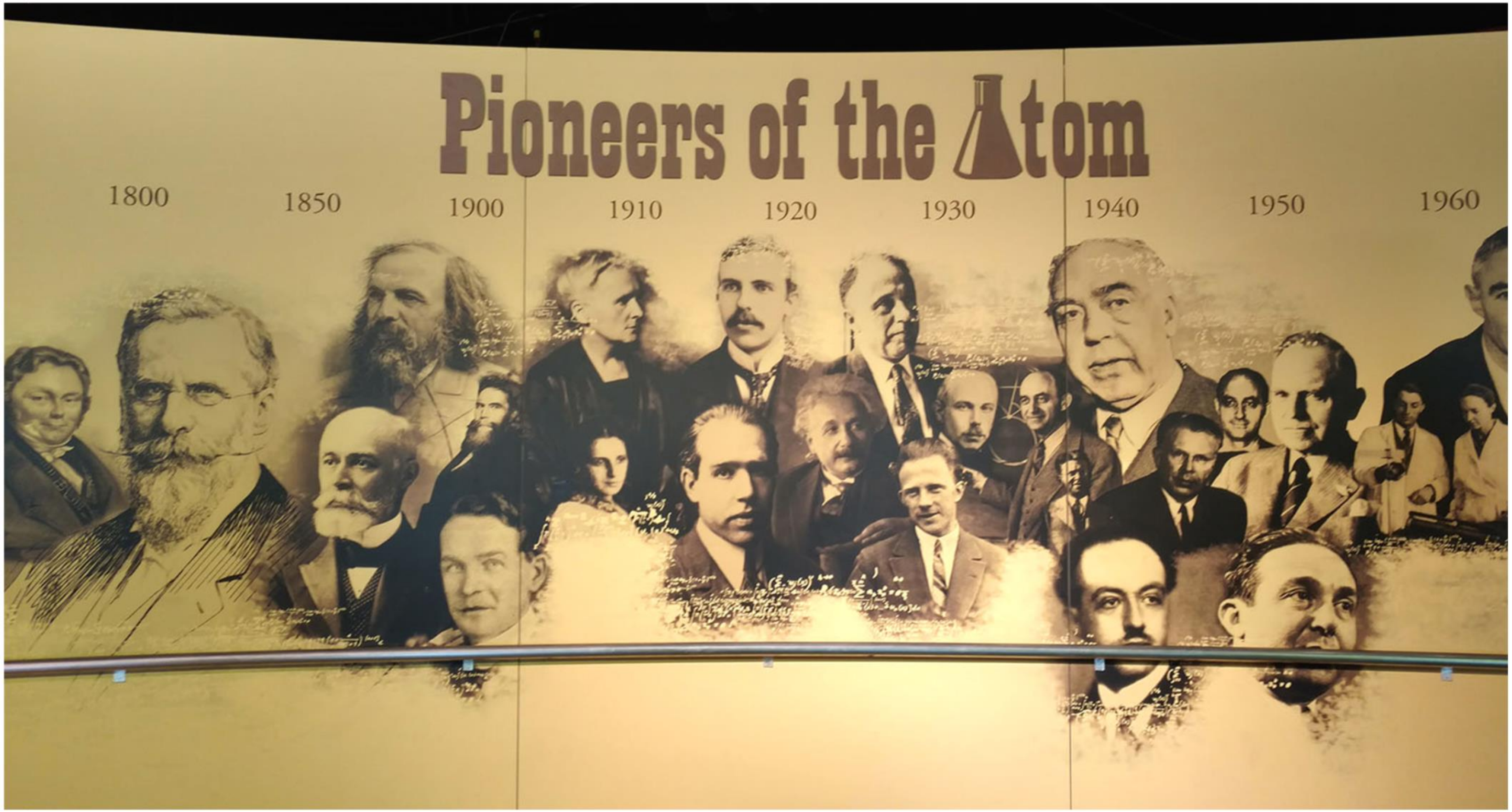
- This **Universe** is divided into two broader categories- A) **Matter** B) **Energy**
- Matter is the anything which occupies space, have mass and perceived by senses.
- We understand matter into **physical** and **chemical** classifications.
- Under **Chemical classification** matter is classified as **“Pure Substances and Impure Substances”**
- Elements are a kind of matter, which comes under types of “Pure Substances”
- Why So? Because **“ELEMENTS” are pure substances consisting of one kind of atoms and are also known to be basic unit of matter.**
- The simplest form of element is **atom.**

What is an atom?

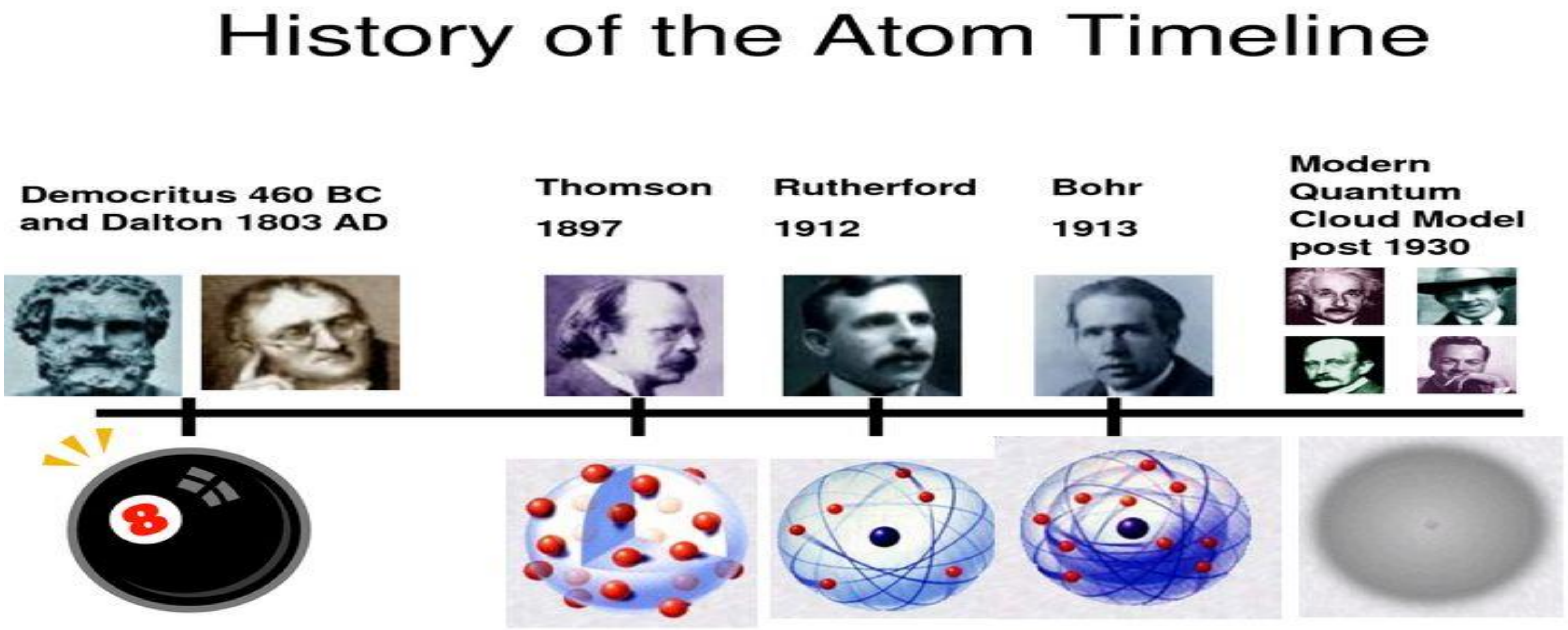


The smallest unit of any element is called an atom.

The atoms of different or same elements are combined to form new substances called compounds and molecules respectively


Pioneers of the Atom
1800
1850
1900
1910
1920
1930
1940
1950
1960

Changes in View of “Atom”

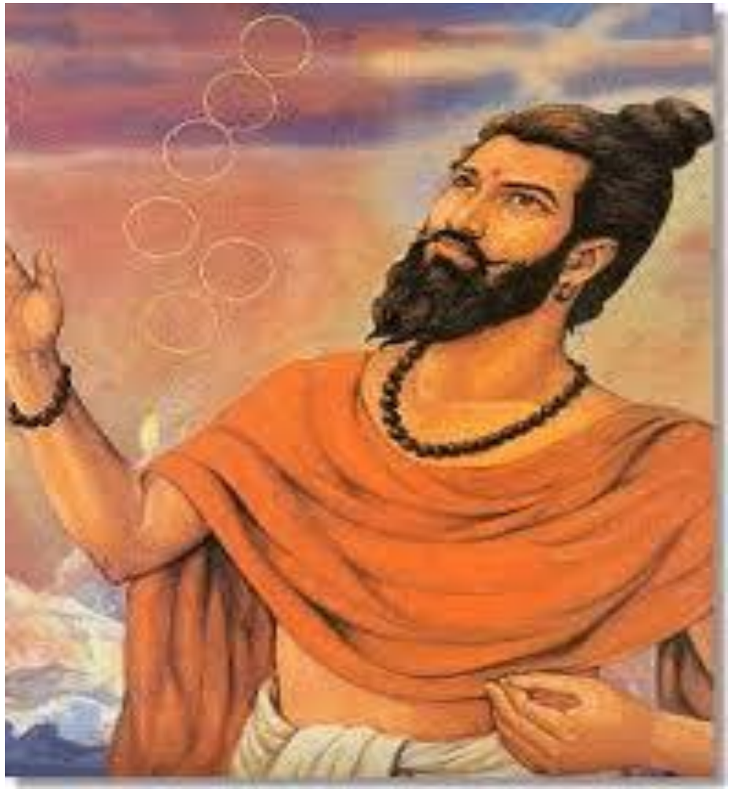


Announcement of existence of Atoms

- The existence of atom has been proposed by ancient Indian & Greek philosopher and Scientist (400 B.C.), who believed that all matter consisted of very small indivisible particles called atoms.
- They said atoms are the fundamental building blocks of matter.
- These ideas were mere speculations and no experimental test or observations are available.
- These ideas were remained dormant for a very long time and revived again by the scientist of nineteenth century.

Indian Scientist and Philosopher Maharishi Kannad

- Proposed that Parmanu (Atom) is an indestructible particle of matter.
- The atom is indivisible because it is a state at which no measurement can be attributed.
- Every object creation is made of atoms (Parmanu) which in turn connect each other to form molecules (annu).
- Atoms are eternal and their combinations constitute the empirical world.



Democritus (400 B.C.)

- **Proposed the matter is composed of tiny indivisible particles.**
- Philosophy, not based on experimental data.
- In Greek - they pronounce atom as Atomos.

John Dalton

- English Scientist, John Dalton was a British school teacher.
- He formulated a precise definition of the indivisible building blocks of matter known as atoms.
- His theory, called as Dalton’s atomic theory.

Dalton’s atomic theory

- Every matter is composed of very minute particles called atoms, which take part in chemical reactions.
- Atoms cannot be further sub divided.
- The atoms of different elements differ from each other in their properties and masses, while the atoms of the same element are identical in all respects.
- The atoms of different elements can combine in simple ratios to form compounds. The masses of combined elements represent the masses of combined atoms.
- Atoms can neither be created nor destroyed.
- In a given compound or molecule the relative number and kind of atoms are constant.

Advantages of Dalton's atomic theory

- Dalton's theory provides us conceptual picture of matter. One can visualize an element as being comprised of tiny particles called atoms.
- It clearly explains that in a compound atoms of two or more elements combine in definite arrangement.
- Mixtures do not involve the intimate interaction between atoms that are found in compounds.
- Dalton's theory embodies several simple laws of chemical combinations that were known at that time, like destructibility of atom indicates law of conservation of mass.
- Combination in compound illustrates law of definite proportion.
- Theory also explains law of multiple proportion and what makes an element to differ from each other.

Limitation's of Dalton's atomic theory

- According to Dalton, smallest particles of elements as well as compounds are atoms, whereas Avogadro's hypothesis explains that smallest particles of a compound is a single molecule.
- Theory could not explain why atoms do combine and form molecules.
- It could not explain the nature of forces which hold the atoms and molecules in solids, liquids and gases.
- It could not explain Gay Lussac's law of combining volumes.
- It couldn't explain that why atoms of the an element differ in their masses.

Evidence for the electrical nature of the atom

- The earliest evidence for the electrical nature of matter came from experiment on frictional electricity. It was found that substances like glass or ebonite when rubbed with silk or fur, generated electricity.
- Although above information did not directly contribute to the understanding of nature of atoms and molecules.
- In 1830 Michael Faraday, an English Physicist, showed that when electricity is passed through the solution of electrolyte, the electrolyte gets decomposed, liberating the deposited matter at the electrodes. This process is known as Electrolysis.
- In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes.

Discovery of Subatomic (Classical) Particles

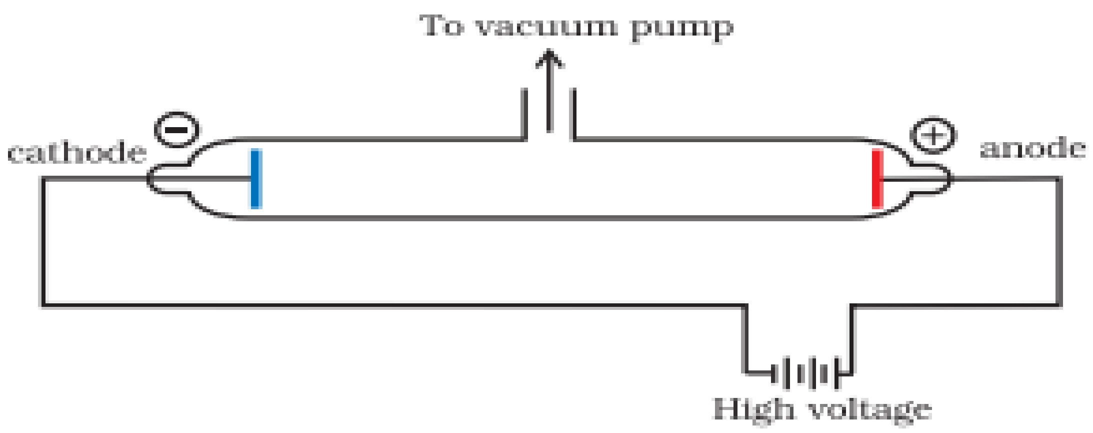
- The laws of electrolysis indicate that atoms involve discrete units of electricity.
- As a result an insight into the structure of atoms was obtained from the experiments on electrical discharge through gases.
- A basic rule regarding the behavior of charged particles: “Like charges repel each other and unlike charges attract each other”.

Discovery of electron

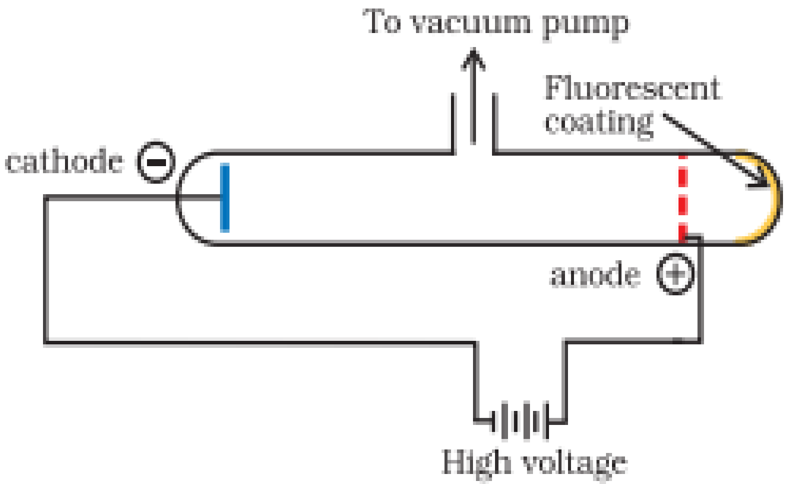
- In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes.
- In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes.

STRUCTURE AND WORKING OF CATHODE RAY TUBE

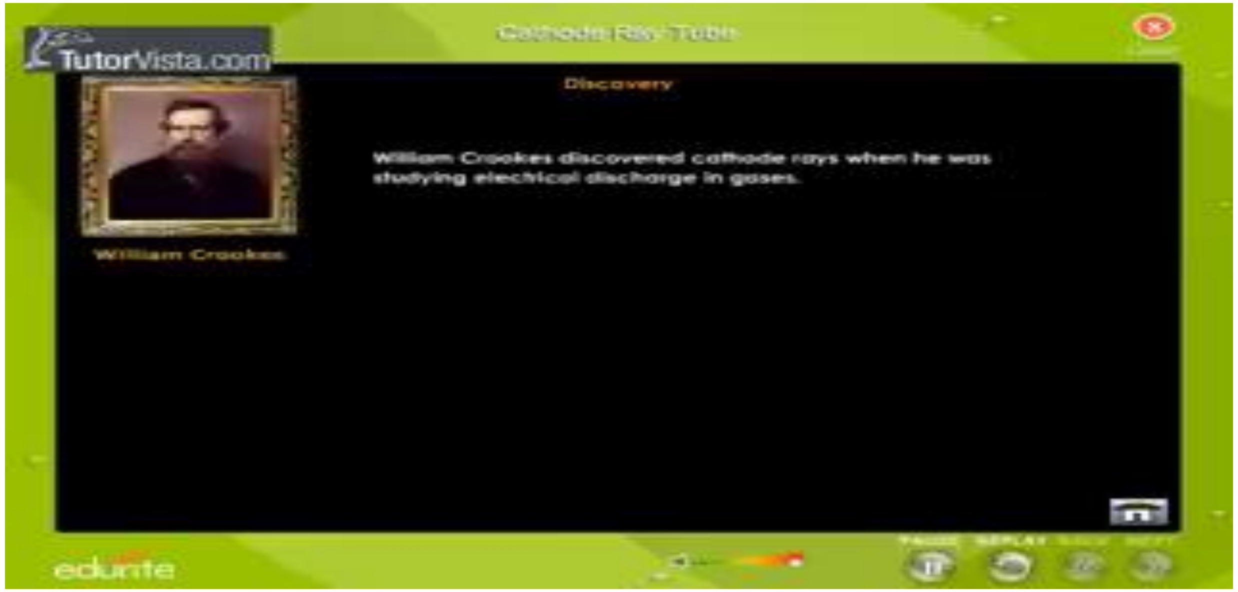
- A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it.
- The electrical discharge through the gases could be observed only at very low pressures and at very high voltages.
- The pressure of different gases could be adjusted by evacuation of the glass tubes.
- When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode).
- These were called cathode rays or cathode ray particles.
- The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating.



A cathode ray discharge tube



A cathode ray discharge tube with perforated anode



Discovery

William Crookes discovered cathode rays when he was studying electrical discharge in gases.

PROPERTIES OF CATHODE RAYS

(i) The cathode rays start from cathode and move towards the anode.

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

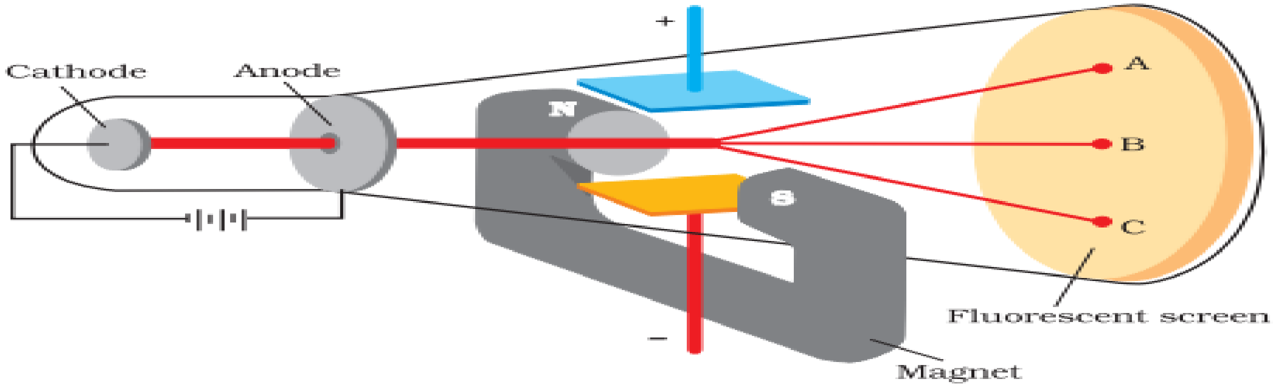
(iii) In the absence of electrical or magnetic field, these rays travel in straight lines.

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called electrons.

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube. Thus, we can conclude that electrons are basic constituent of all the atoms.

Charge to Mass Ratio of Electron

- In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (me) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons.
- When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A.
- Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path which is followed in the absence of electric or magnetic field and they hit the screen at point B.



The apparatus to determine the charge to the mass ratio of electron

The amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.

(ii) the mass of the particle — lighter the particle, greater the deflection.

(iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

Thomson was able to determine the value of e/me as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\ \mathrm{C\ kg^{-1}}$$

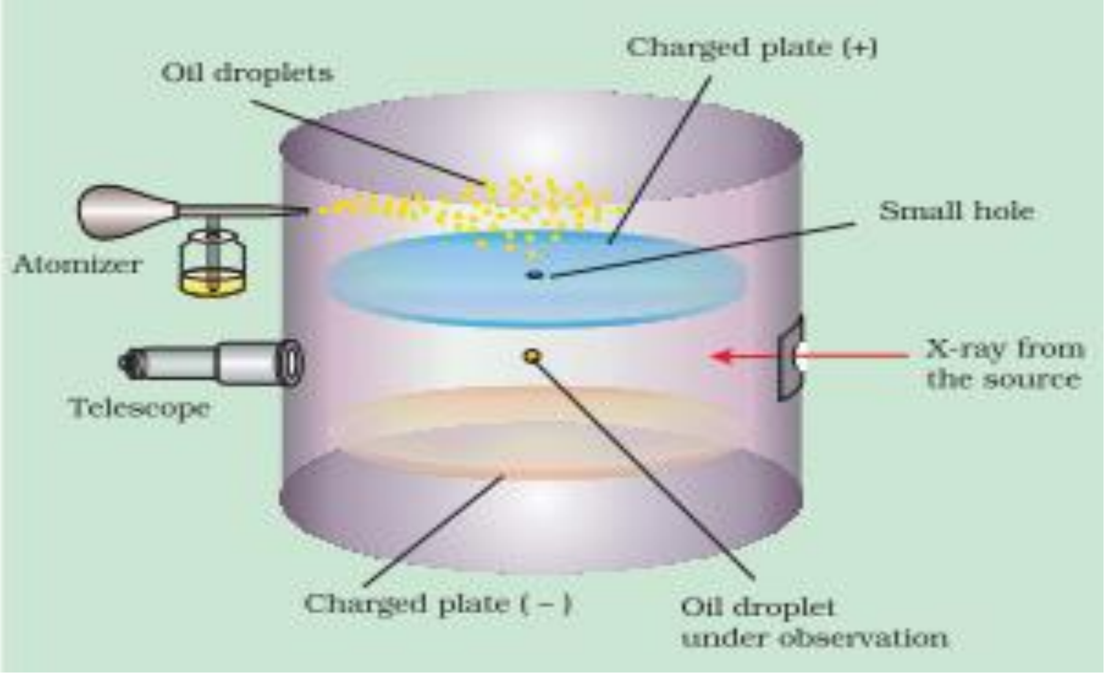
Where me is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is –ve.

Charge on the Electron

- R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons.
- He found the charge on the electron to be -1.6×10^{-19} C.
- The present accepted value of electrical charge is $-1.602176 \times 10^{-19}$ C.
- The mass of the electron (me) was determined by combining these results with Thomson’s value of e/me ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.602176 \times 10^{-19}\,\mathrm{C}}{1.758820 \times 10^{11}\,\mathrm{C\,kg^{-1}}}$$

$$= 9.1094 \times 10^{-31}\,\mathrm{kg}$$



The Millikan oil drop apparatus for measuring charge 'e'.

In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.

ROBERT MILLIKAN
1896 - 1926

In 1906, Robert Millikan was able to determine the value of the charge on the electron in his "oil drop" experiment.

- Millikan’s Oil Drop Method In this method, oil droplets in the form of mist, produced by the atomizer, were allowed to enter through a tiny hole in the upper plate of electrical condenser.
- The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece.
- By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets.
- The air inside the chamber was ionized by passing a beam of X-rays through it.
- The electrical charge on these oil droplets was acquired by collisions with gaseous ions.
- The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate.
- By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, q = n e, where n = 1, 2, 3... .

Discovery of Protons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of canal rays carrying positively charged particles.

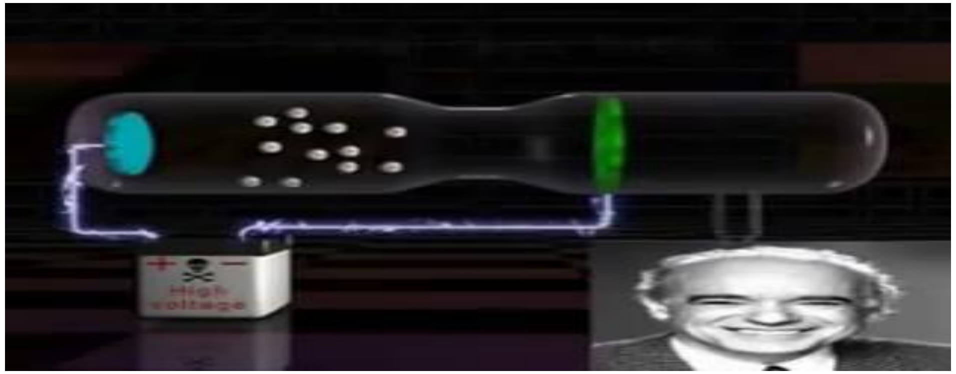
The characteristics of these positively charged particles are listed below:

(i) Unlike cathode rays, mass of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

(ii) The charge to mass ratio of the particles depends on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.



Properties of Anode Rays or Canal Rays

- Anode rays travel in straight line
- Anode rays consist of material particles
- Anode rays are deflected by electric field towards negatively charged plates
- Anode rays get deflected under the influence of magnetic field also.
- Unlike cathode rays, the positively charged particles depend upon nature of gas present in side the discharge tube, because these are simply the positively charged ions.
- The mass of positive rays depends upon the atomic weights or molecular weights of the gases in the discharge tube.
- The e/m ratio also varies because the change in positive charge on the rays. It may be either equal to or the integral multiple of the charge of the electron.
- The lightest of all particles identified in positive rays from different elements was one with the mass very slightly less than that of hydrogen atom or nearly equals to hydrogen atom.
- The lightest positively charged particle is called a proton.
- Rays produce flashes of light on ZnS screen.
- These rays can pass through thin metal foil and can produce ionization in gases.

Note

- e/m ratio will be maximum when when hydrogen gas is in the discharge tube. This shows that positive ions formed from hydrogen are lightest. So, hydrogen ions are considered as proton and later in 1911 named by Rutherford.
- The charge to mass ratio (e/m) for protons is 9.58×10^{4} C/gm, which is maximum value of e/m observed for any +ve particle.
- The charge on protons has the same magnitude as that of electrons but opposite sign, i.e. 1.6022×10^{-19} C.
- From the above two values mass of the proton is found to be 1.67×10^{-24} gm or 1.67×10^{-27} kg.

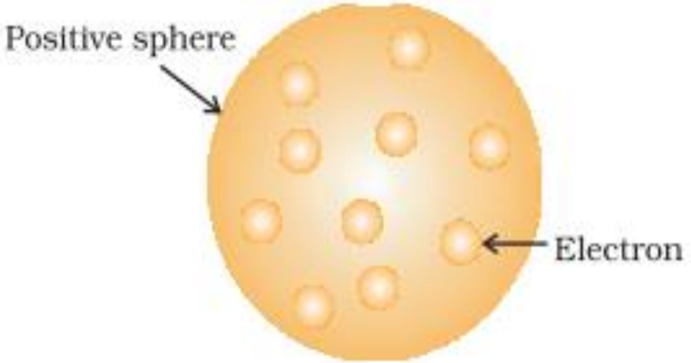
Conclusion

- A sub atomic particle, which is fundamental constituent of all matter, have a mass almost equals to H-atom and which carries a positive charge equal in magnitude to the charge of electron, is called proton.
- It is denoted by **“p or p^+ or $^1p_1$”**.
- In the discharge tube when gases gets ionised they removed electrons, the removed electrons are the constitutes of cathode rays and ionised gaseous ions form canal rays.
- **Example:** $H \rightarrow H^+ (Positive\ rays) + \ e^- \ (Cathode\ rays) \rightarrow e/1amu(\frac{Charge}{mass})$

ATOMIC MODELS

- **Thomson Model of Atom**
- **Rutherford’s Nuclear Model of Atom**

Thomson Model of Atom

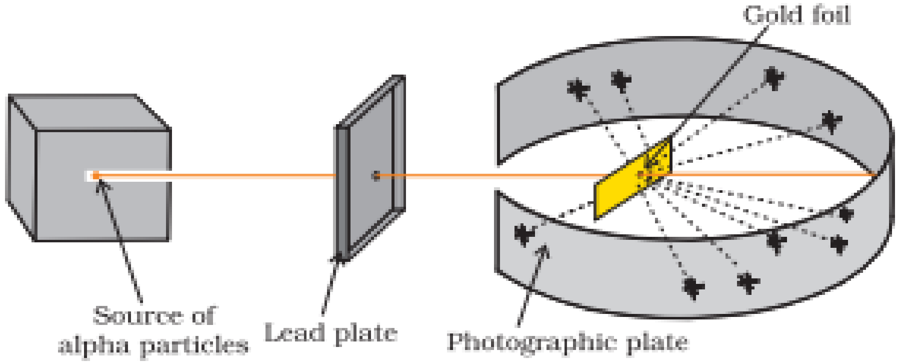


- J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10–10 m) in which the positive charge is uniformly distributed.
- The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement.
- Many different names are given to this model, for example, plum pudding, raisin pudding or watermelon.

An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments.

Rutherford’s Nuclear Model of Atom

- Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles.
- A stream of high energy α–particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal.
- The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point.



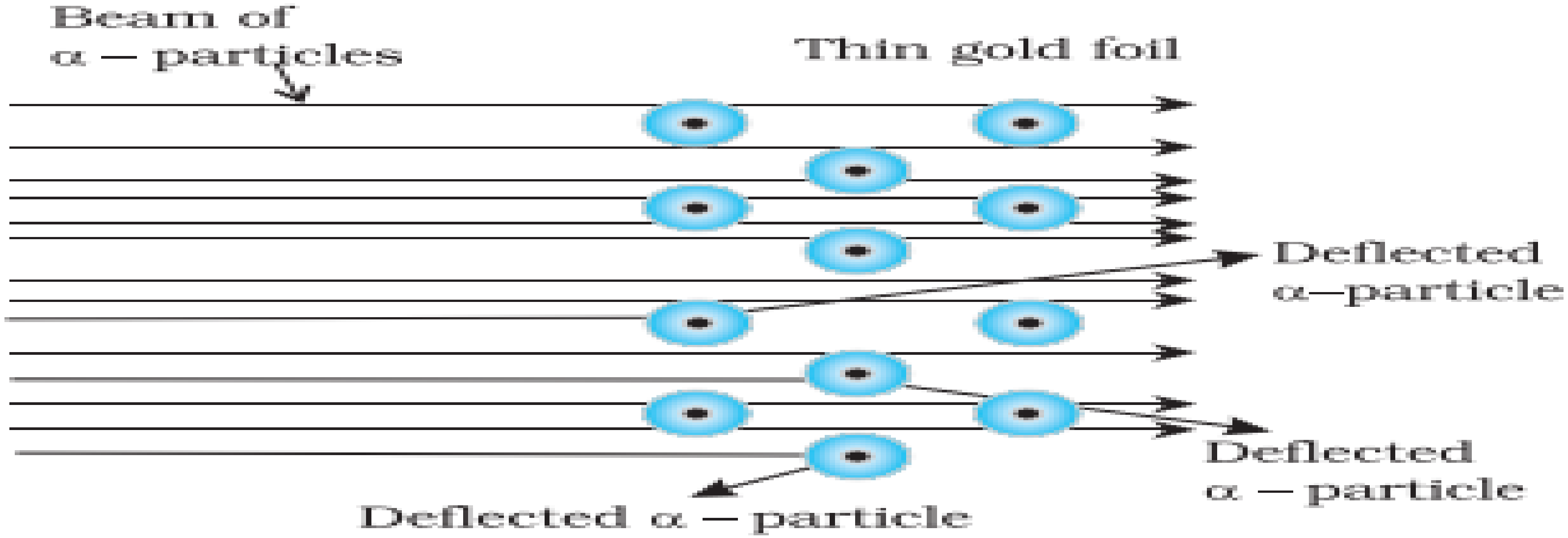
Rutherford’s scattering experiment

Observations:

(i) most of the α–particles passed through the gold foil undeflected.

(ii) a small fraction of the α–particles was deflected by small angles.

(iii) a very few α–particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°



Schematic molecular view of the gold foil

Conclusions

(i) Most of the space in the atom is empty as most of the α–particles passed through the foil undeflected.

(ii) A few positively charged α–particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α–particles.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realizing that if it represents a nucleus, then the radius of atom would be about 5 km.

On the basis of observations and conclusions, Rutherford proposed the nuclear model of atom:

(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus by Rutherford.

(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.

(iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks of Rutherford Model

- **According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10–8 s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.**
- **Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons.**

Discovery of Neutron

- It is a remarkable fact the *existence of neutron was not discovered until 1932*. The general atomic imagination of the time was protons and electrons. Through *Rutherford's alpha scattering experiments*, it was found out that the Atomic mass number A of an element is a bit more than twice the atomic number Z for most atoms and that essentially all the mass of an atom was concentrated in a very tiny space at the center of the atom. The alpha particles that took a 180-degree turn stand as proof to this.
- Until 1930, a few electrons were thought to coexist with the protons in the dense nucleus but the immense amount of energy required to sustain such a system was way beyond the atomic energies. If we take the size of a Hydrogen atom as 0.2 nanometers, then the electron confinement energy is 38eV which is the correct magnitude for atomic electrons. But if the electron were to coexist with the protons in the nucleus, the electron confinement energy is approximately 250Mev! Many magnitudes huger than the 38eV.

- A breakthrough came when it was shown that the bombardment of Beryllium with alpha particles from a radioactive source yielded penetrating but non-ionizing radiation. Such neutral radiation confounded the scientists since the only known neutral radiation than were photos. The neutral radiation had it been a photon would exit the beryllium atom with far more energy than it actually does.
- The answer to this puzzle was provided by **James Chadwick** who boldly stated that this was a new type of fundamental particle which is neutral and he called them **Neutrons**. From the conservation of energy and momentum, he was able to derive with considerable accuracy the mass of this new particle. He found that the mass of a neutron was very close to that of a proton.

$$\mathbf{M_N} = 1.00866 \text{ u} = 1.6749 \text{ X } 10^{-27} \text{ kg}$$

- So now the nucleus had another resident, and the proton-neutron pair was called a Nucleon. The discovery of Neutron led to a better understanding of atomic mass and atomic number also with isotopes which is what radioactivity is based on.

Some Important Terms & Definitions

- **Atomic Number**
- **Mass Number**
- **Isotopes**
- **Isobars**
- **Isotones**
- **Isoelectronic**

Atomic Number and Mass Number

Atomic number (Z) = number of protons in the nucleus of an atom = number of electrons in a neutral atom

Mass number (A) = number of protons in the nucleus of an atom
+
number of neutrons in the nucleus of an atom

The proton-neutron pair was called a **Nucleon**.

For example, the nucleus of a Uranium atom is represented by a $^{235}_{92}U$ which means that one atom of Uranium 235 contains 235 nucleons, of which 92 are protons and the rest 143 are neutrons.

Isotopes

- Isotopes are variants of a particular element with different a different number of neutrons. For example, the two isotopes of Uranium are, $^{235}{}_{92}$ U and $^{239}{}_{92}$ U. You will see here that the number of protons is the same in both the isotopes but they contain 143 and 147 neutrons respectively. The presence of an extra neutron significantly changes the behaviour of that particular atom. There are two different types of isotopes, stable and radioactive. Stable isotopes are one that can exist in its free state without breaking down spontaneously. Radioactive isotopes are ones that are too unstable to sustain itself and they spontaneously break down into two lighter daughter elements with the emission of particles such as alpha, beta and gamma rays.
- For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called protium ($^{1}{}_{1}$H). Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1 neutron is called deuterium ($^{2}{}_{1}$D, 0.015%) and the other one possessing 1 proton and 2 neutrons is called tritium ($^{3}{}_{1}$T). The latter isotope is found in trace amounts on the earth. Other examples of commonly occurring isotopes are: carbon atoms containing 6, 7 and 8 neutrons besides 6 protons

($^{12}{}_{6}$C, $^{13}{}_{6}$C, $^{14}{}_{6}$C); chlorine atoms containing 18 and 20 neutrons besides

17 protons ($^{35}{}_{17}$Cl, $^{37}{}_{17}$Cl).

NOTE:

Isotopes is that chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus. Number of neutrons present in the nucleus have very little effect on the chemical properties of an element. Therefore, all the isotopes of a given element show same chemical behaviour.

- **Isobars** are elements that have the same number of nucleons (sum of protons and neutrons). The series of elements with 40 Mass number serves as a good example; ${}^{40}_{16}S$, ${}^{40}_{17}Cl$, ${}^{40}_{18}Ar$, ${}^{40}_{19}K$, and ${}^{40}_{20}Ca$. The nucleus of all the above-mentioned elements contain the same number of particles in the nucleus but contain varying numbers of protons and neutrons.

- **Isotones** are atoms that have the same neutron number but different proton number. For example, ${}^{36}_{16}S$, ${}^{37}_{17}Cl$, ${}^{38}_{18}Ar$, ${}^{39}_{19}K$ and ${}^{40}_{20}Ca$ are all isotones of 20 since they all contain 20 neutrons.
- **Isoelectronic** refers to two atoms, ions or molecules that have the same electronic structure and the same number of valence electrons. The term means "equal electric" or "equal charge". Isoelectronic chemical species typically display similar chemical properties. Atoms or ions with the same electronic configurations are said to be isoelectronic to each other or to have the same isoelectronicity.

Example: The K^+ ion is isoelectronic with the Ca^{2+} ion. The carbon monoxide molecule (CO) is isoelectronic to nitrogen gas (N_2) and NO^+.

Nature of electromagnetic radiation and atomic spectra

- Nature of light
- Atomic spectra
- Defects of Rutherford's model

Nature of light

- Corpuscular theory
- Wave theory
- Electromagnetic spectrum
- Planck's quantum theory of radiation
- Photo electric effect
- Dual nature of light

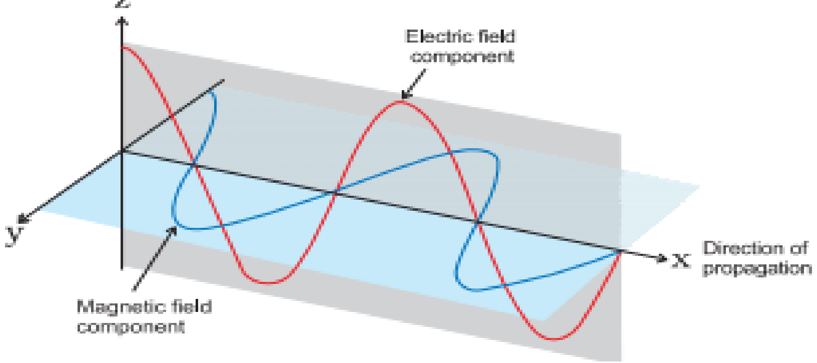
Corpuscular theory

- Light is a particular form of energy. In order to explain the nature of light, Newton proposed a theory known as **Corpuscular Theory.**
- **According to this theory light is composed of tiny particles known as corpuscles.**
- This theory successfully explained the phenomenon of reflection and refraction but failed to explain the phenomenon of interference and diffraction. Therefore, this theory could not stand for a long time and was rejected.

The Wave Theory of Light

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.

A Wave in Water When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.



- James Maxwell (1870) was the first to give a comprehensive explanation about the interactio between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called electromagnetic waves or electromagneti radiation.
- Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character.
- The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutuall perpendicular planes.

The main points of this theory are:

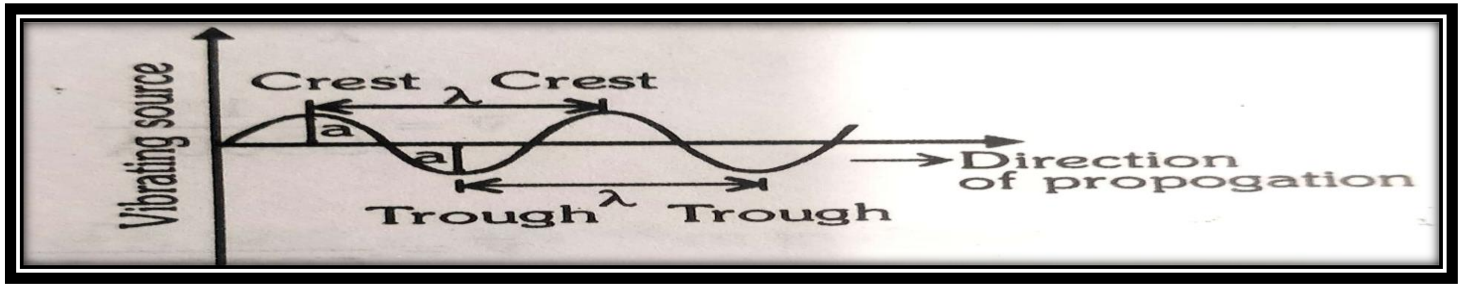
1)The energy is emitted from any source continuously in the form of radiations and is called the **radiant energy.**

2)The radiations consist of electric and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of propagation of the radiation.

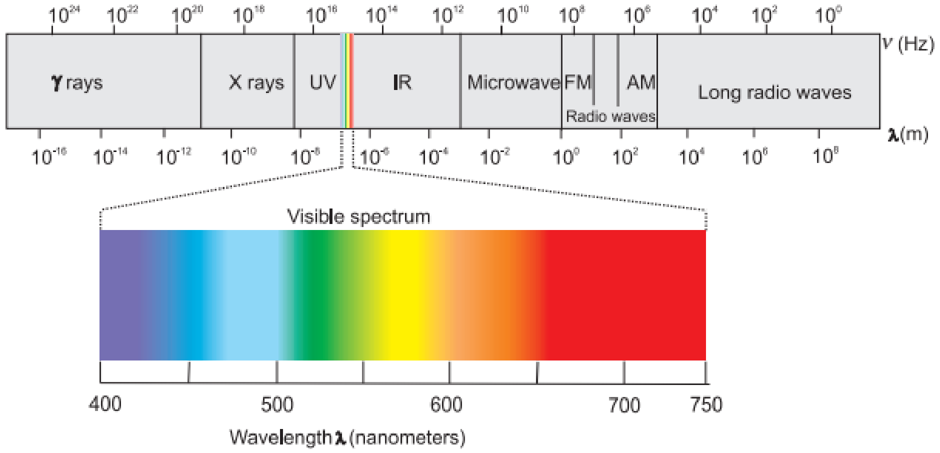
3)The radiations possesses wave character and travel with the velocity of light.

The radiations are called **electromagnetic radiations or electromagnetic waves.**

4)These waves do not require any material medium for propagation.



Electromagnetic spectrum



The spectrum of electromagnetic radiation

Electromagnetic spectrum

- There are many types of electromagnetic radiations which differ from one and another in wavelength or frequency.
- These constitute electromagnetic spectrum.
- Different regions of spectrum are identified by different names.
- Eg: Radio frequency region is around 10^6 Hz, used for broad casting, microwave region around 10^{10} Hz used for radar etc.

1)Wavelength

- Wavelength of a wave is defined as the distance between any two consecutive crest or trough.
- It is represented by **λ** (Lambda) and is expressed in A° or m or cm or nm or pm.
- 1 A° = 10^{-8} cm = 10^{-10} m

2)Frequency

- Frequency of a wave is defined as the number of waves passing through a point in 1 seconds.
- It is represented by **ν** (nu) and is expressed in hertz(Hz) or cycles/second or sec^{-1}

3)Velocity

- Velocity of a wave is defined as the linear distance travelled by the wave in 1 seconds.
- It is represented by **c** and is expressed in cm/sec or m/sec.

4)Amplitude

- Amplitude of a wave is the height of the crest or the depth of the trough.
- It is represented by **a** and is expressed in the units of length.

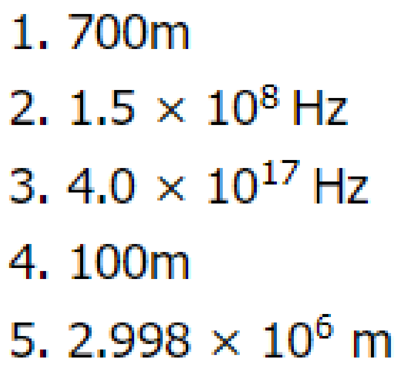
5)Wavenumber $\bar{\nu}$

- Wavenumber is defined as the number of waves present in 1 cm length.
- It will be equal to the reciprocal of the wavelength.

Problems

1. What is the wavelength of a wave with a frequency of 4.28 Hz?
2. What is the frequency of a wave with a wavelength of 200 cm?
3. What is the frequency of a wave with a wavelength of 500 pm?
4. What is the wavelength of a wave with a frequency of 2.998×10^5 Hz?
5. A radio transmits a frequency of 100 Hz. What is the wavelength of this wave?

Answers:



1. 700m
2. 1.5×10^8 Hz
3. 4.0×10^{17} Hz
4. 100m
5. 2.998×10^6 m

Planck's Quantum Theory: Quantization Of Energy

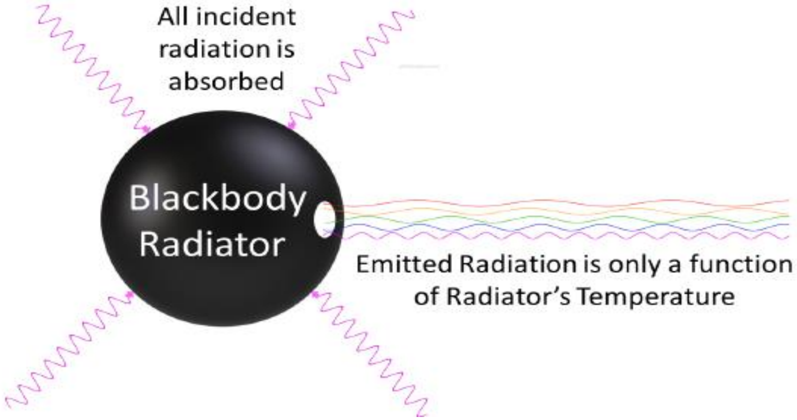
Maxwell’s suggestion about the wave nature of electromagnetic radiation was helpful in explaining the phenomena such as interference, diffraction etc. However, he failed to explain various other observations such as the nature of emission of radiation from hot bodies, photoelectric effect i.e. ejection of electrons from a metal compound when electromagnetic radiation strikes it, the dependence of heat capacity of solids upon temperature, line spectra of atoms (especially hydrogen).

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton’s laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell’s equation, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

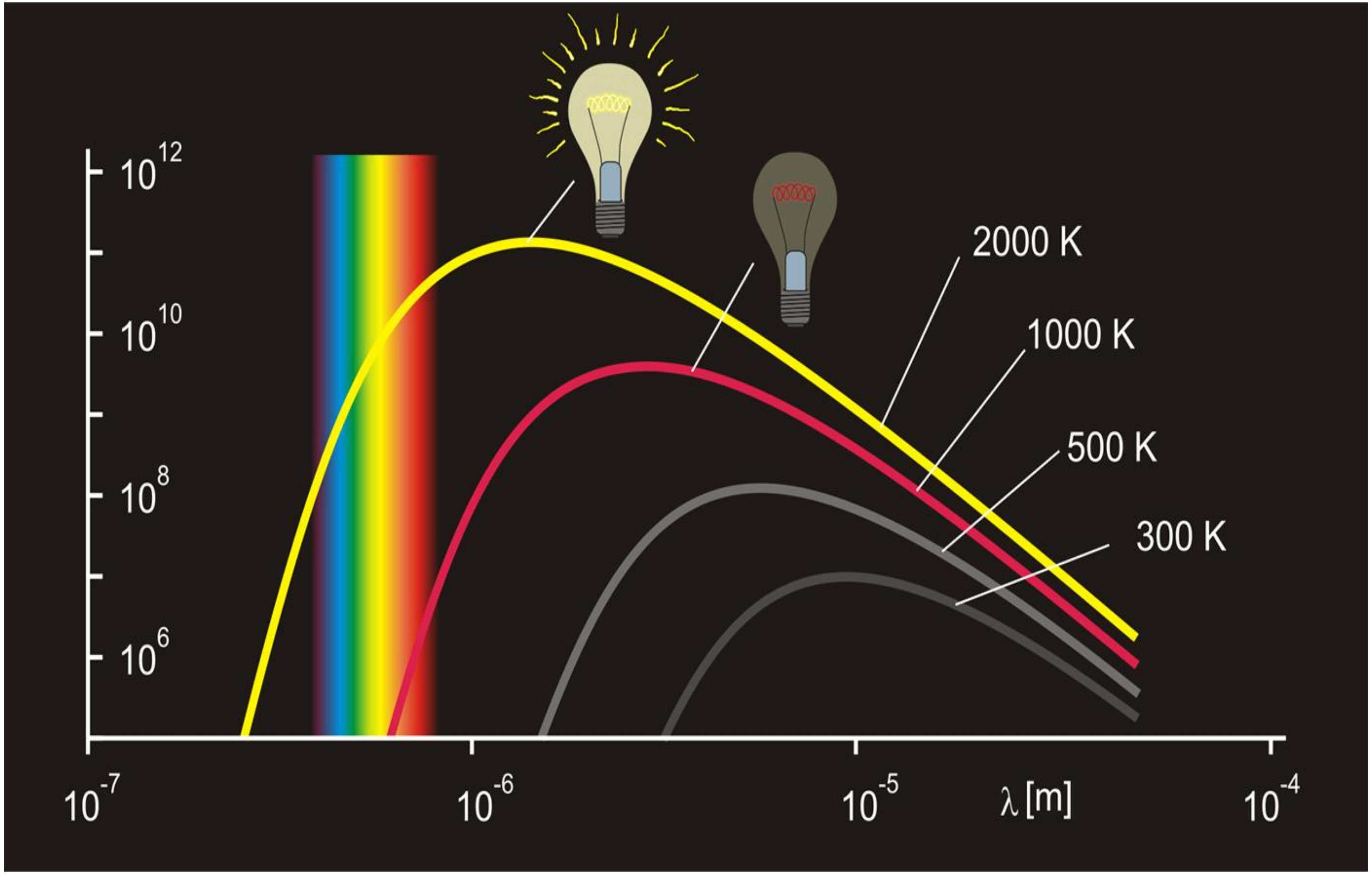
One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation. Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity actually drops to zero at short wavelengths, the Rayleigh-Jeans result was called the “ultraviolet catastrophe.” There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

Black Body Radiation

- Solids, when heated, emit radiation varying over a wide range of wavelengths. For example: when we heat solid color, changes continue with a further increase in temperature. This change in color happens from a lower frequency region to a higher frequency region as the temperature increases. For example, in many cases, it changes from red to blue. An ideal body which can emit and absorb radiation of all frequencies is called a black body. The radiation emitted by such bodies is called black body radiation.
- Thus, we can say that variation of frequency for a black body radiation depends on the temperature. At a given temperature, the intensity of radiation is found to increase with an increase in the wavelength of radiation which increases to a maximum value and then decreases with an increase in the wavelength. This phenomenon couldn't be explained with the help of Maxwell's suggestions. Hence, Planck proposed the Planck's quantum theory to explain this phenomenon.


All incident radiation is absorbed
Blackbody Radiator
Emitted Radiation is only a function of Radiator's Temperature

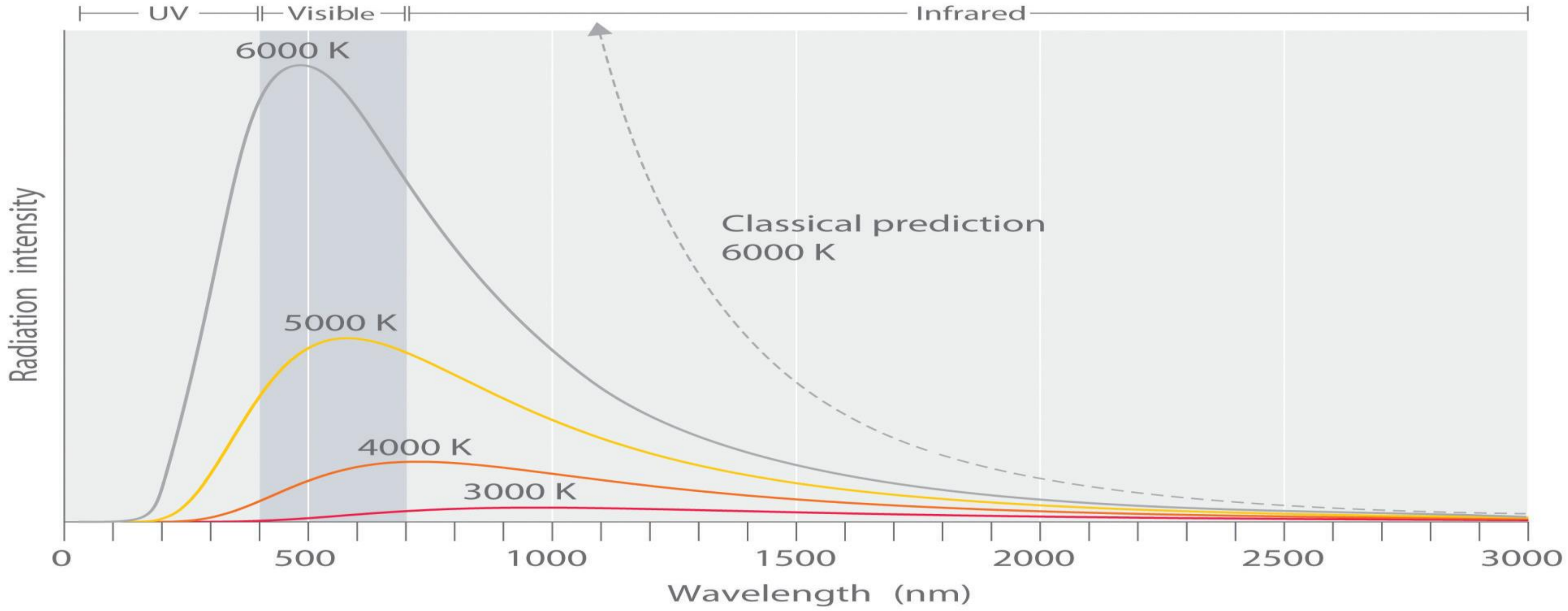
Intensity



Wavelength

Quantizing Electrons in the Radiator

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks. So the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.



Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.

Quantization

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion may have a charge of −1 or −2, but *not* −1.33 electron charges.

According to Planck's quantum theory,

- Different atoms and molecules can emit or absorb energy in discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.
- The energy of the radiation absorbed or emitted is directly proportional to the frequency of the radiation.

Meanwhile, the energy of radiation is expressed in terms of frequency as,

$$E = h\nu$$

Where,

E = Energy of the radiation

h = Planck's constant (6.626×10^{-34} J.s)

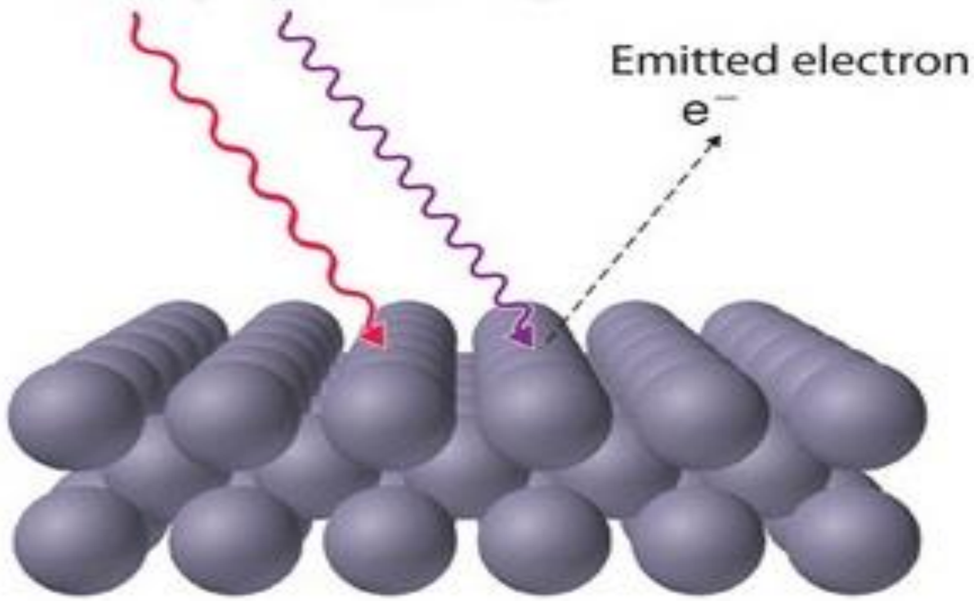
ν= Frequency of radiation

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data .

We can understand Planck’s explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

The Photoelectric Effect

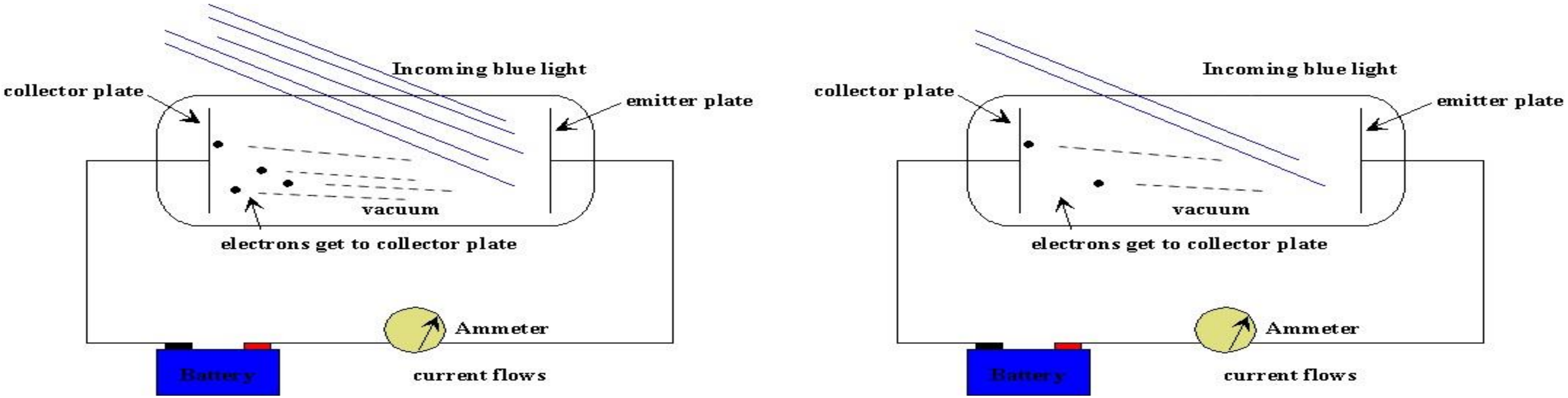
The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (also called photoelectrons) leaving the metal's surface by J.J. Thomson.



Sodium metal in a vacuum

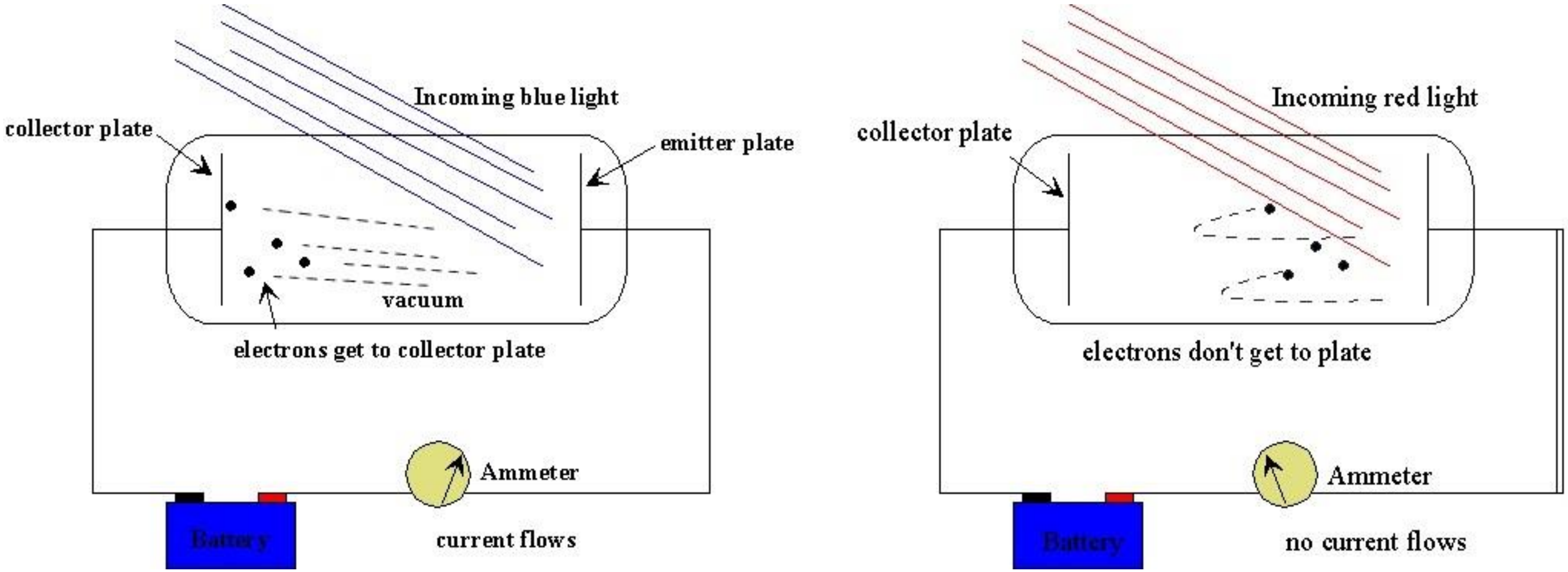
- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

Intensity Dependence



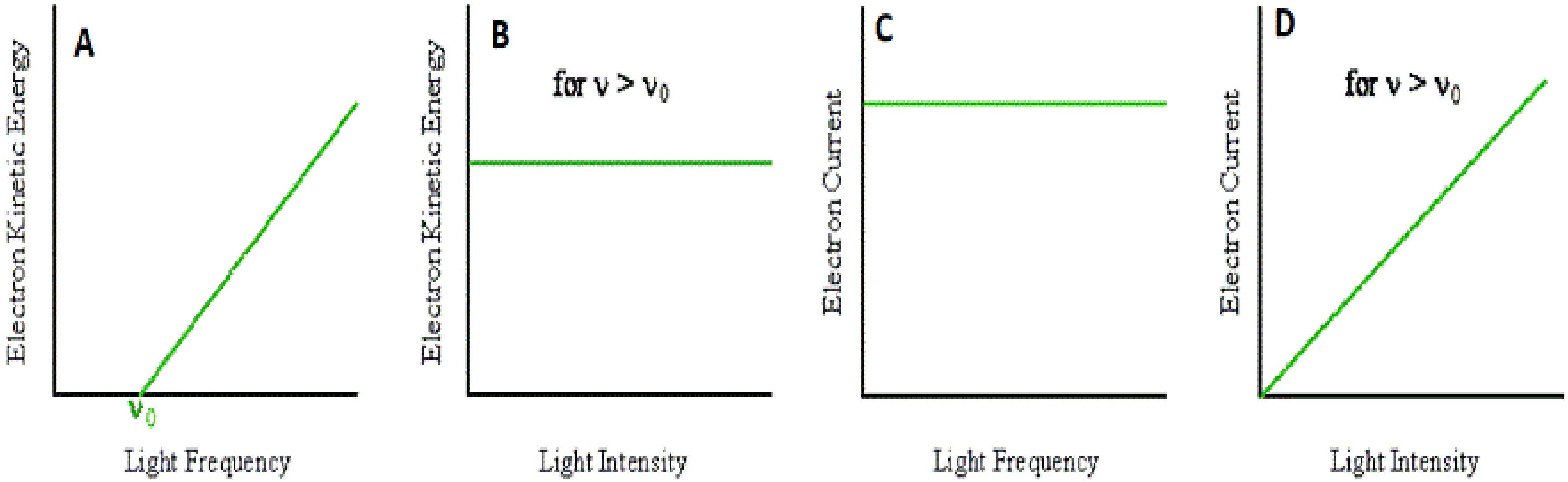
Millikan's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity.

Wavelength Dependence



Millikan's photoelectric experiment (left) High-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than $\mathbf{V_{stop}}$, for blue light. (right) Low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds $\mathbf{V_{stop}}$ for red light.

- The kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of **ν_0** (no current is observed below **ν_0**) and the kinetic energy is independent of the intensity of the radiation, and
- The number of electrons (i.e. the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of **ν_0** (i.e., no current is observed below **ν_0**)



Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy **hν**, with **ν** the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, this is usually called the work function, **Φ**. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy.

$$\text{K.E.} = h\nu - \Phi$$

According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum frequency ν_0 *needed to eject an electron with no residual energy.*

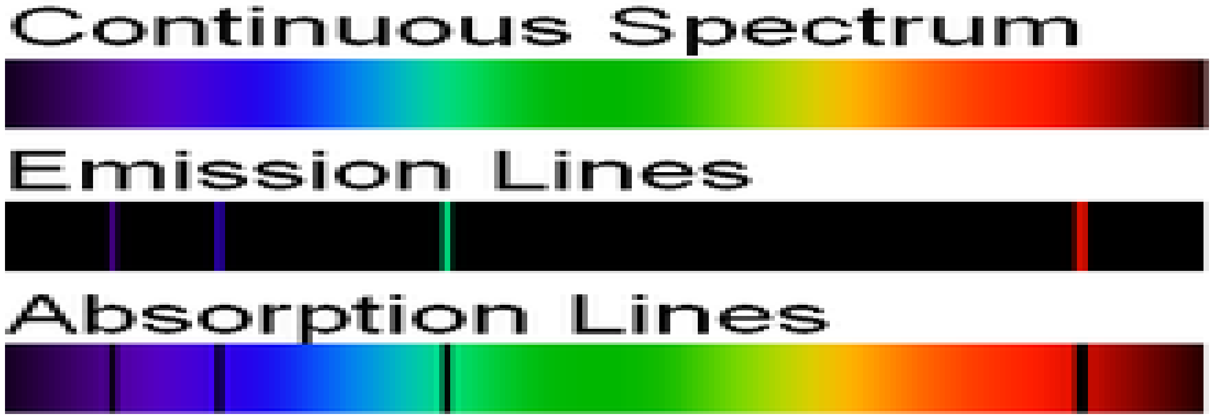
Atomic Spectra

In an atom, electrons have discrete and specific energies. There are more energy states in an atom than there are electrons. When an electron transitions from one energy level to another, it emits light or photon with a specific wavelength.

In any given set of conditions, the collection of all these specific wavelengths is what constitutes the atomic spectrum. Hence, atomic spectra are the spectra of atoms

What is Atomic Spectra?

When an electron gets excited from one energy level to another, it either emits or absorbs light of a specific wavelength. The collection of all these specific wavelengths of the atom in a given set of conditions like pressure, temperature, etc. is the atomic spectra of atoms. There are three types of atomic spectra and they are emission spectra, absorption spectra, and continuous spectra.



Difference Between Emission And Absorption Spectra

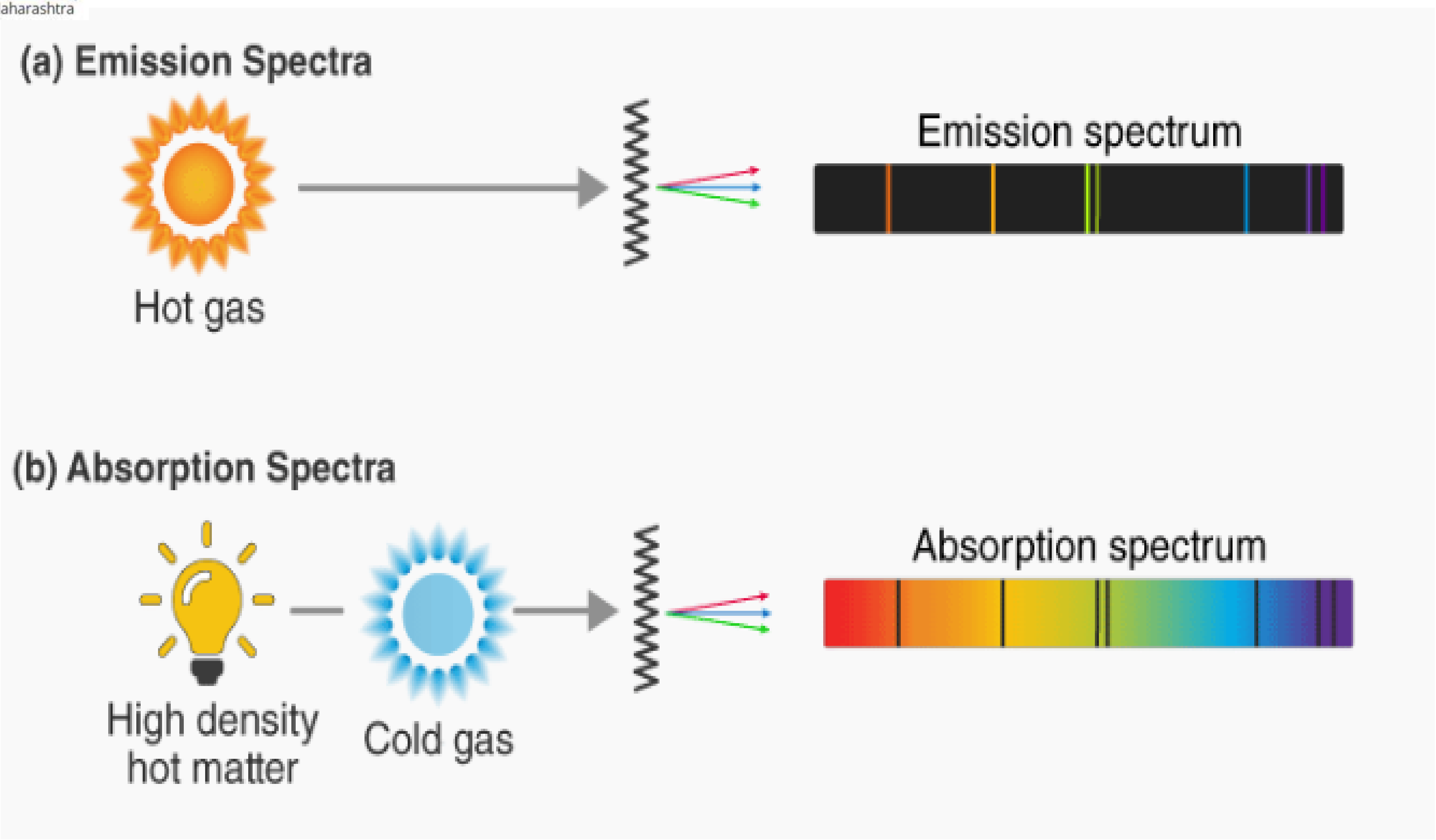
What is emission spectrum?

When energy is absorbed by electrons of an atom, electrons move from lower energy levels to higher energy levels. However, these electrons have to emit energy to return to their ground state from the excited state which is unstable. The frequencies of light emitted in such cases form the emission spectrum.

e

What is absorption spectrum?

On the other hand, an absorption spectrum is constituted by the frequencies of light transmitted with dark bands when energy is absorbed by the electrons in the ground state to reach higher energy states.


(a) Emission Spectra
Hot gas
Emission spectrum
(b) Absorption Spectra
High density hot matter
Cold gas
Absorption spectrum

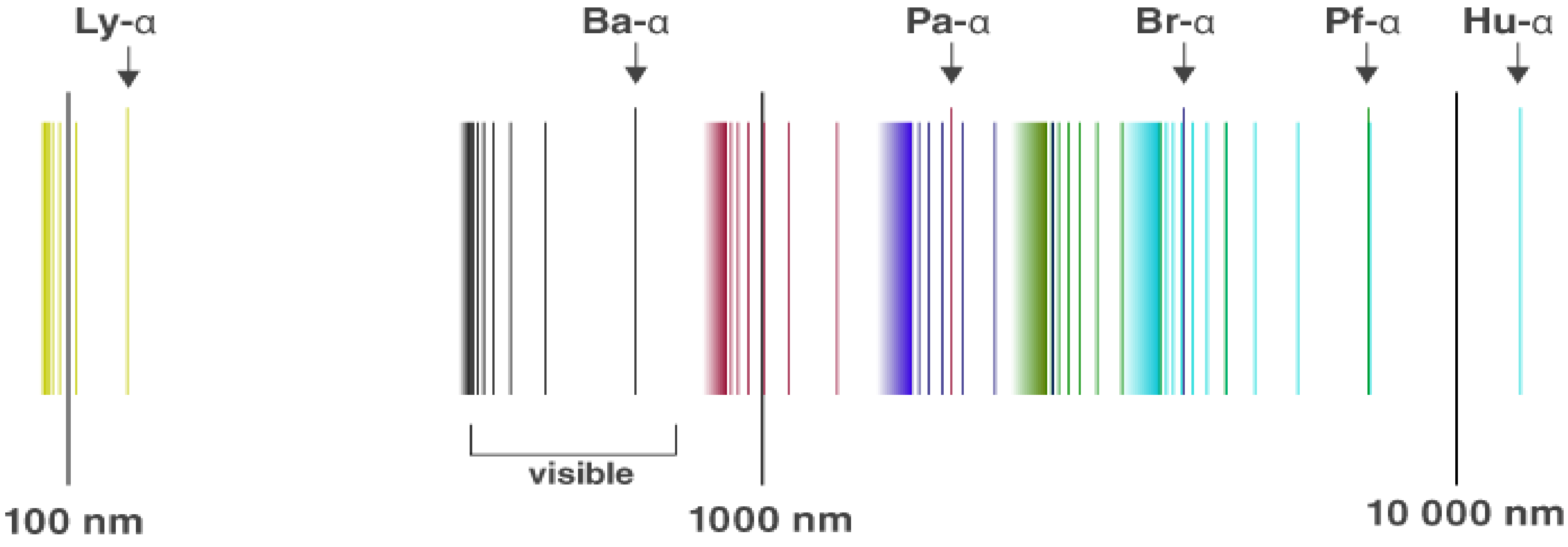
Emission Spectra VS Absorption Spectra

The main difference between emission and absorption spectra is that an emission spectrum has different coloured lines in the spectrum whereas an absorption spectrum has dark coloured lines in the spectrum.

Emission Spectra	Absorption Spectra
Produced when atoms release energy	Produced when atoms absorb energy
Comprise of coloured lines in the spectrum	Comprise of dark lines or gaps in the spectrum
Is in helpful in figuring out the composition of a certain matter	Can be used to figure out the ability of certain objects to retian heat and its absorption level
The type of photons emitted is helpful in figuring out the kind of elements the substance is made of as each element radiates a different amount of energy and has a unique emission level	The wavelengths of light absorbed is helpful in figuring out the quantity of substances in the sample.

Spectral Series of Hydrogen Atom

It is evident that the atomic hydrogen emission spectrum is divided into a number of spectral lines with wavelengths given by the Rydberg formula. The observed spectral lines in the hydrogen emission spectrum are due to the atomic transitions between different energy levels. The spectral series are important in astronomical spectroscopy.



Hydrogen spectral series

Rydberg Formula

Using the Rydberg formula, it becomes easy to calculate the spectral lines. Following is the formula:

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

Lyman series with $n_1 = 1$

Balmer series with $n_1 = 2$

Paschen series (or Bohr series) with $n_1 = 3$

Brackett series with $n_1 = 4$

Pfund series with $n_1 = 5$

Humphreys series with $n_1 = 6$

Where,

- ***R*** is the Rydberg constant ($1.09737*10^{7}$ m^{-1})
- ***Z*** is the atomic number
- ***n*** is the upper energy level
- ***n'*** is the lower energy level
- ***λ*** is the wavelength of light

Note: Spectral series of single-electron atoms like hydrogen have Z = 1.

Atomic Spectroscopy

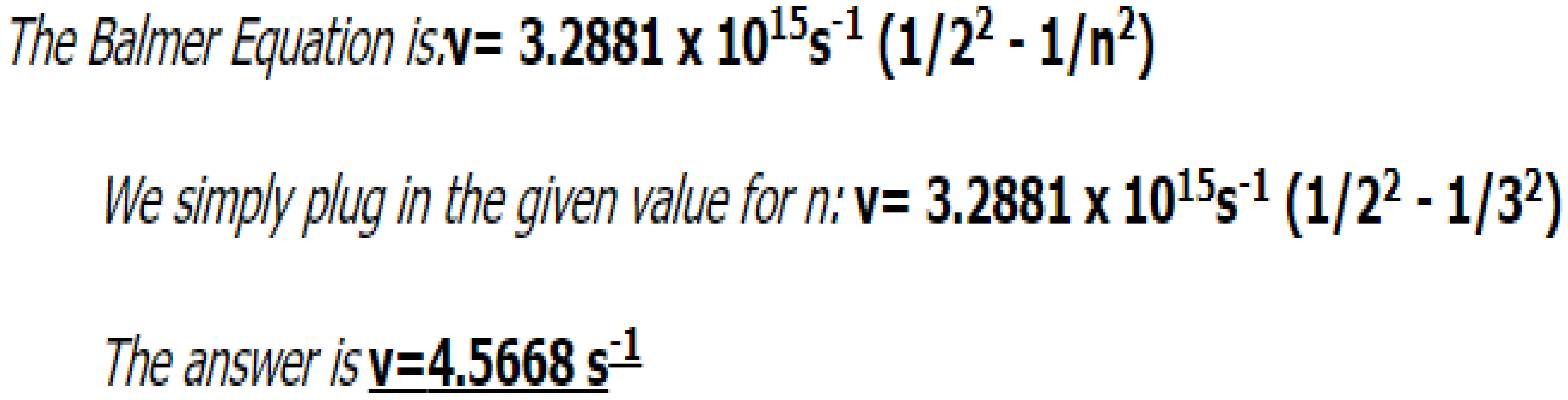
- Atomic spectroscopy is the study of the electromagnetic radiation absorbed or emitted by the atoms. There are three types of atomic spectroscopy and they are:
- Atomic emission spectroscopy: This involves the transfer of energy from the ground state to an excited state. The electronic transition can be explained in atomic emission.
- Atomic absorption spectroscopy: For absorption to take place there should be identical energy difference between the lower and higher energy levels. The atomic absorption spectroscopy principle uses the fact that the free electrons generated in an atomizer can absorb radiation at specific frequency. It quantifies the absorption of ground-state atoms in the gaseous state.
- Atomic fluorescence spectroscopy: This is a combination of atomic emission and atomic absorption as it involves radiation of both excitation and de-excitation.

Uses of Atomic Spectroscopy

- It is used for identifying the spectral lines of materials used in metallurgy.
- It is used in pharmaceutical industries to find the traces of materials used.
- It can be used to study multidimensional elements.

1. Using the Balmer equation, find the frequency of the radiation corresponding to n=3.

Solution



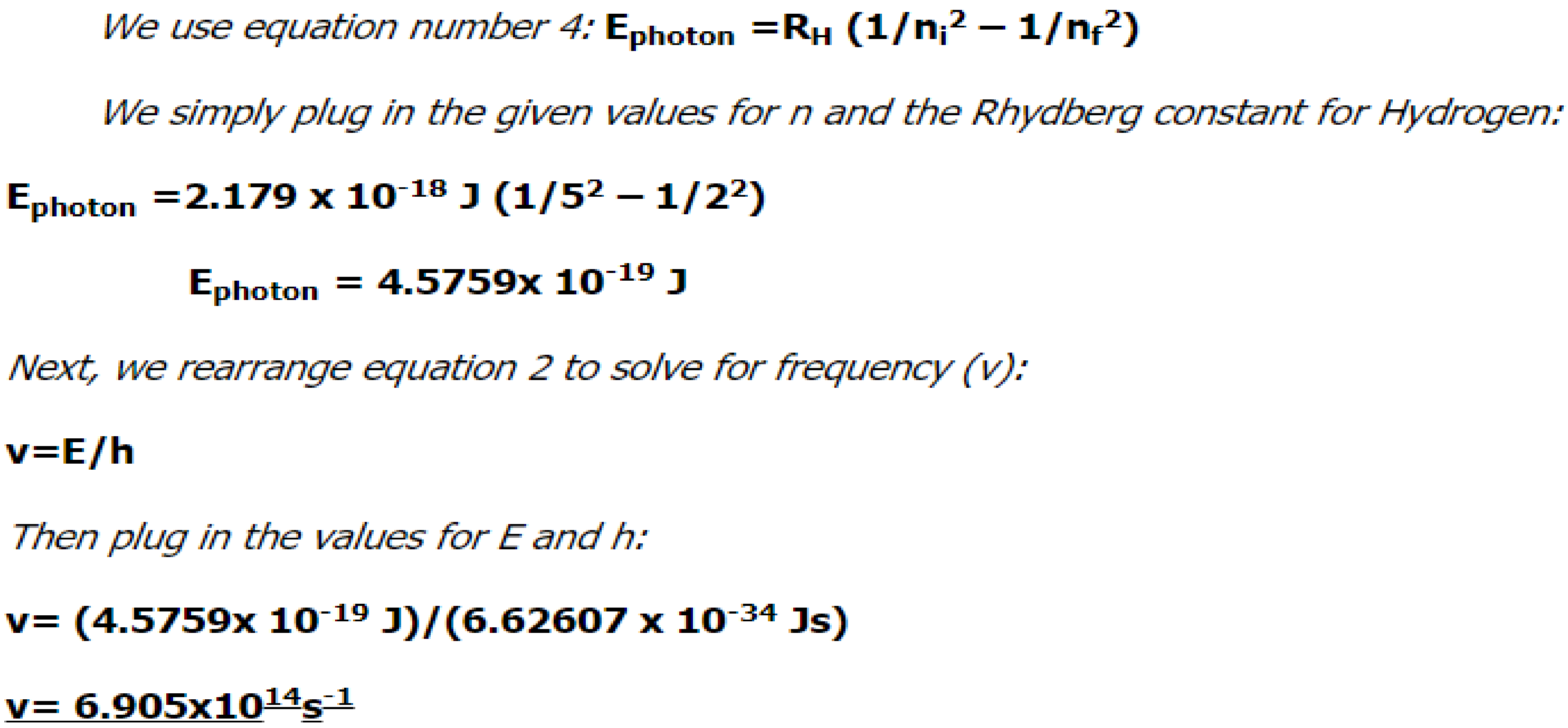
The Balmer Equation is: $v = 3.2881 \times 10^{15} s^{-1} (1/2^2 - 1/n^2)$

We simply plug in the given value for n: $v = 3.2881 \times 10^{15} s^{-1} (1/2^2 - 1/3^2)$

The answer is $\underline{v = 4.5668\ s^{-1}}$

2. What is the frequency of the spectral line produced when an electron moves from n=5 to n=2 in a Hydrogen atom?

Solution



We use equation number 4: $\mathbf{E_{photon} = R_H\ (1/n_i^2 - 1/n_f^2)}$

We simply plug in the given values for n and the Rhydberg constant for Hydrogen:

$\mathbf{E_{photon} = 2.179 \times 10^{-18}\ J\ (1/5^2 - 1/2^2)}$

$\mathbf{E_{photon} = 4.5759 \times 10^{-19}\ J}$

Next, we rearrange equation 2 to solve for frequency (v):

$\mathbf{v = E/h}$

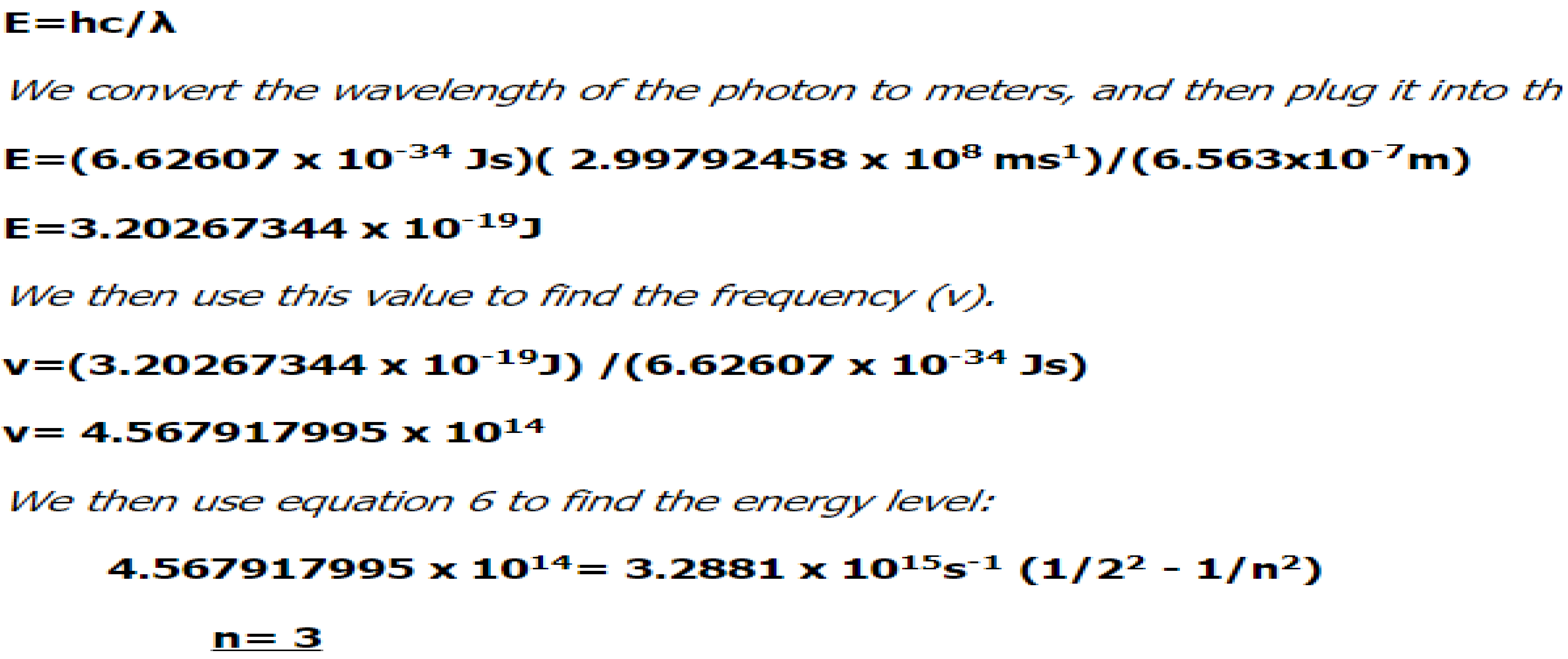
Then plug in the values for E and h:

$\mathbf{v = (4.5759 \times 10^{-19}\ J)/(6.62607 \times 10^{-34}\ Js)}$

$\underline{\mathbf{v = 6.905 \times 10^{14} s^{-1}}}$

3. What value of n does the line at 656.3 nm in the Balmer series correspond to?

Solution



$E = hc/\lambda$

We convert the wavelength of the photon to meters, and then plug it into th

$E = (6.62607 \times 10^{-34}\ Js)(\ 2.99792458 \times 10^{8}\ ms^{1})/(6.563 \times 10^{-7} m)$

$E = 3.20267344 \times 10^{-19} J$

We then use this value to find the frequency (v).

$v = (3.20267344 \times 10^{-19} J)\ /(6.62607 \times 10^{-34}\ Js)$

$v = 4.567917995 \times 10^{14}$

We then use equation 6 to find the energy level:

$4.567917995 \times 10^{14} = 3.2881 \times 10^{15} s^{-1}\ (1/2^{2} - 1/n^{2})$

$\underline{n = 3}$

4. A photon with a wavelength of 397nm is emitted from an electron in energy level 7 of a Hydrogen atom. What is the new energy level of the electron?

Solution

We use equation number 3 ($E_n = -R_H/n^2$)to find the number of joules when n=7:

$E_7 = (2.179 \times 10^{-18}\ J)/7^2$

$E_7 = -4.4469388 \times 10^{-20}\ J$

We then substitute equation 1 into equation 2 to get this equation:

$E=hc/\lambda$

We convert the wavelength of the photon to meters, and then plug it into the equation

$E_{photon} = (6.62607 \times 10^{-34}\ Js)(\ 2.99792458 \times 10^{8}\ ms^{-1})/(3.97 \times 10^{-7} m)$

$E_{photon} = 5.00358898 \times 10^{-19}\ J$

We then subtract the energy of the photon emitted from the energy level the electron was originally in; this will give us the energy of the new energy level:

$E_{n\ final} = E_{n\ initial} - E_{photon}$

Plug the values previously calculated into the equation:

$E_{n\ final} = (-4.4469388 \times 10^{-20} J) - (5.00358898 \times 10^{-19}\ J)$

$E_{n\ final} = -5.4482829 \times 10^{-19} J$

*To figure out the energy level (n), we can plug our **$E_{n\ final}$** into equation number 3:*

$E_n = -R_H/n^2$

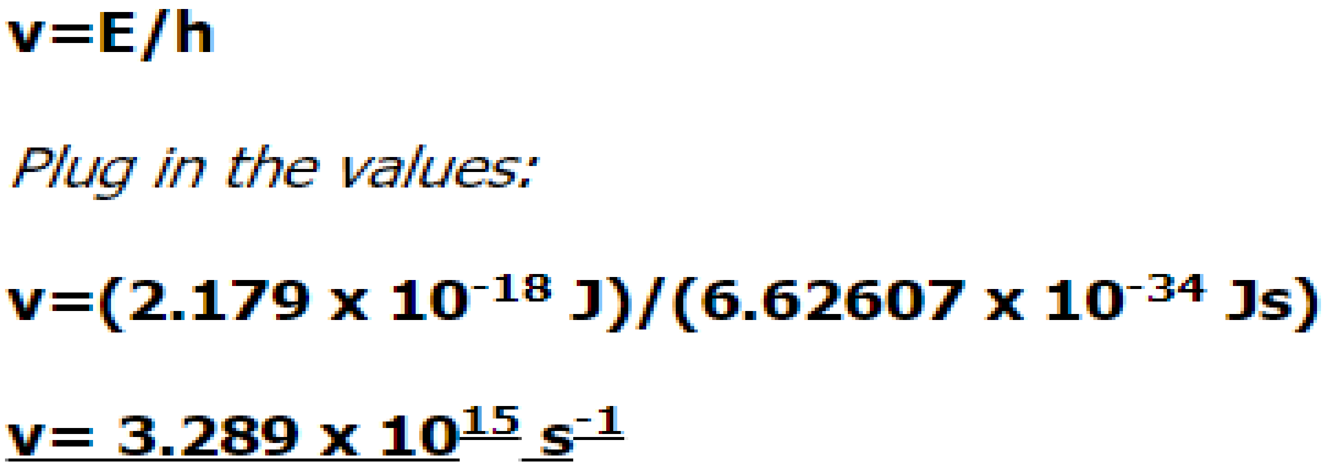
$-5.4482829 \times 10^{-19} J = (-2.179 \times 10^{-18}\ J)/n^2$

We solve for n, and get:

$\underline{n=2}$

5. Find the frequency in Hertz of radiation with an energy of $2.179 x 10^{-18}$ J per photon.

Solution



$v=E/h$

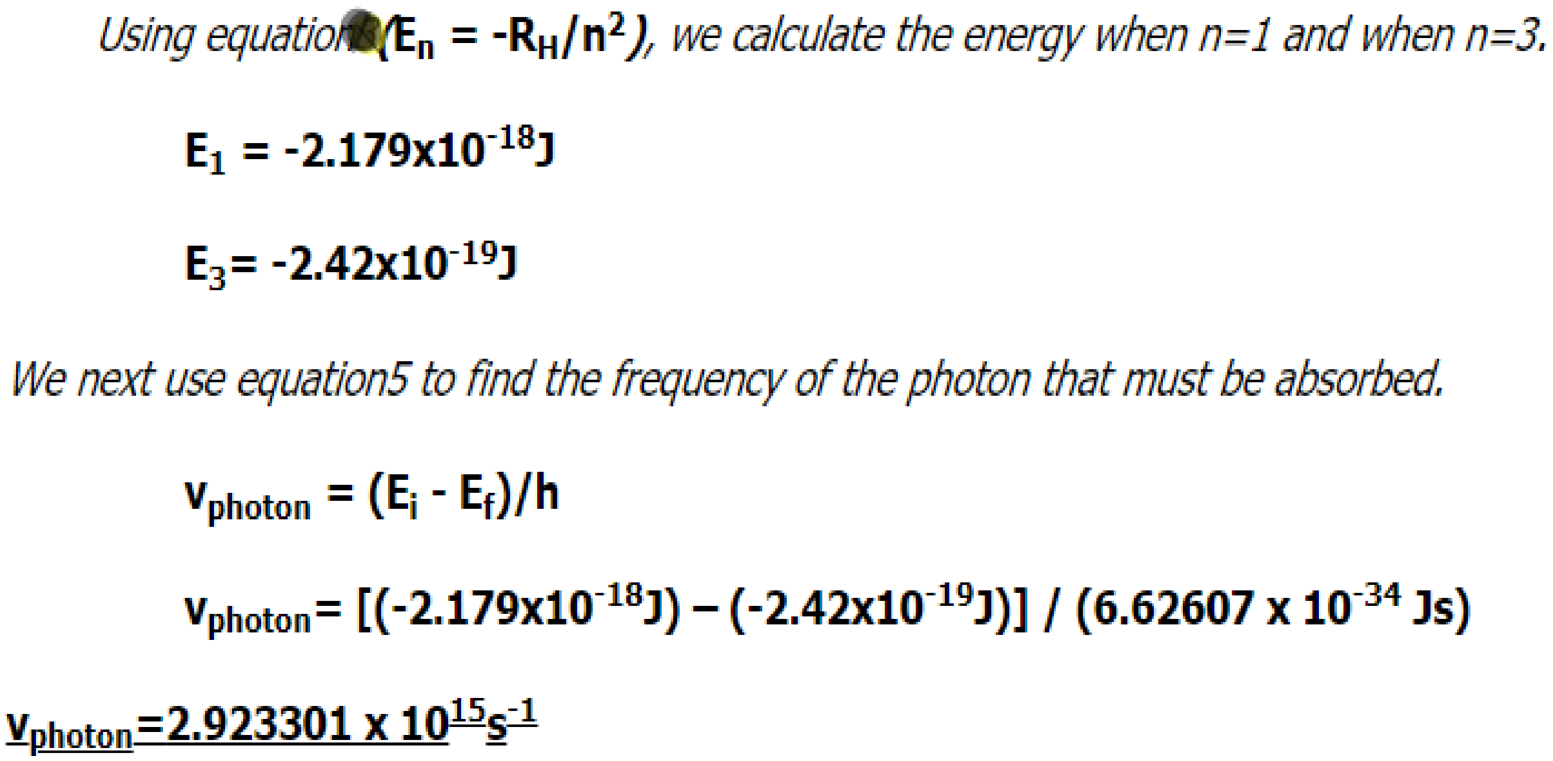
Plug in the values:

$v=(2.179 \text{ x } 10^{-18} \text{ J})/(6.62607 \text{ x } 10^{-34} \text{ Js})$

$\underline{v= 3.289 \text{ x } 10^{15} \text{ s}^{-1}}$

6. What frequency of light would be needed to make an electron in a Hydrogen atom jump from n=1 to n=3 ?

Solution



Using equations ($E_n = -R_H/n^2$), *we calculate the energy when n=1 and when n=3.*

$E_1 = -2.179\text{x}10^{-18}\text{J}$

$E_3 = -2.42\text{x}10^{-19}\text{J}$

We next use equation5 to find the frequency of the photon that must be absorbed.

$\nu_{photon} = (E_i - E_f)/h$

$\nu_{photon} = [(-2.179\text{x}10^{-18}\text{J}) - (-2.42\text{x}10^{-19}\text{J})] / (6.62607 \times 10^{-34}\ \text{Js})$

$\underline{\nu_{photon} = 2.923301 \times 10^{15} s^{-1}}$

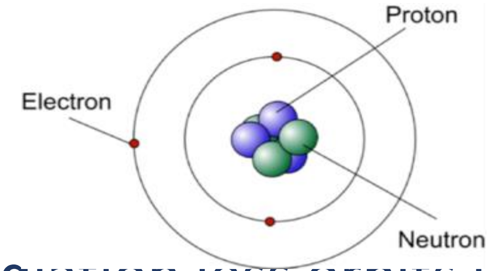
7. A spectral line is measured to have a wavelength of 1000nm. Is this within the Balmer series?

Solution

No, the Balmer series does not extend into the infrared.

Bohr model

Bohr Model was introduced after the Rutherford's model. It retained some of the features like the orbiting of nucleus and the electrons under the action of the Coulomb's Law of electrostatic attraction. Various other concepts like radiation less orbits and stationary states were also introduced in the Bohr Model. We discuss the postulates of Bohr Atomic theory.



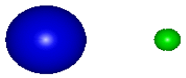
Bohr introduced the concept of radiation less orbits in which the electrons revolve as usual around the nucleus but without radiating any kind of energy which is contrary to the laws of electromagnetism. This was a hypothesis, but at least a working one.

Radiation occurred only when an electron made a transition from one stationary state to another. The difference between the energies of the two states was radiated as a **single photon**. Absorption occurred when a transition occurred from a lower stationary state to a higher stationary state.

He also introduced the correspondence principle which states that the spectrum is continuous and the frequency of light emitted equals the frequency of the electron.

Neil Bohr explained the line spectrum while developing the model of an atom. We discuss the various postulates of the Bohr Atomic Model.

1. The Bohr model shows that the electrons in atoms are in orbits of differing energy around the nucleus. The electron in an atom has only certain definite stationary states of motion allowed to it, called as energy levels. Each energy level has a definite energy associated with it. In each of these energy levels, electrons move in circular orbit around the positive nucleus. The necessary centripetal force is provided by the electrostatic attraction of the protons in the nucleus. As one moves away from the nucleus, the energy of the levels increases.

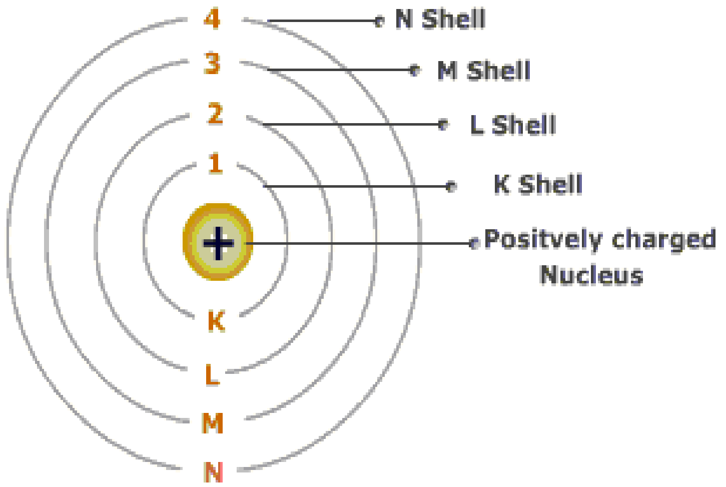


2. The energy level occupied by an electron usually **is called the ground state**. It may move to a lev of higher energy or a less stable shell by **absorbing energy**. This higher energy but less stable shell level is termed as the excited state of the electron.

3. These states of allowed electronic motion are those in which the **angular momentum of an electron** is **an integral multiple of h/2π** or one can say that the angular momentum of an electro quantized.

Angular Momentum

$$mvr = \frac{nh}{2\pi}$$



where m is the mass, v is the velocity, r is the radius of the orbit, h is Planck's constant and n is a positive integer.

- When an atom is in one of these states, it does not radiate any energy but whenever there is a transition from one state to other, energy is emitted or absorbed depending upon the nature of transition.
- After reaching the state of excitation, the electron can return to its original ground state by releasing the **energy it has absorbed**.
- Sometimes the energy released by electrons occupies the portion of the electromagnetic spectrum (the range of wavelengths of energy) that humans detect as visible light. Slight variations in the amount of the energy are seen as light of different colors.

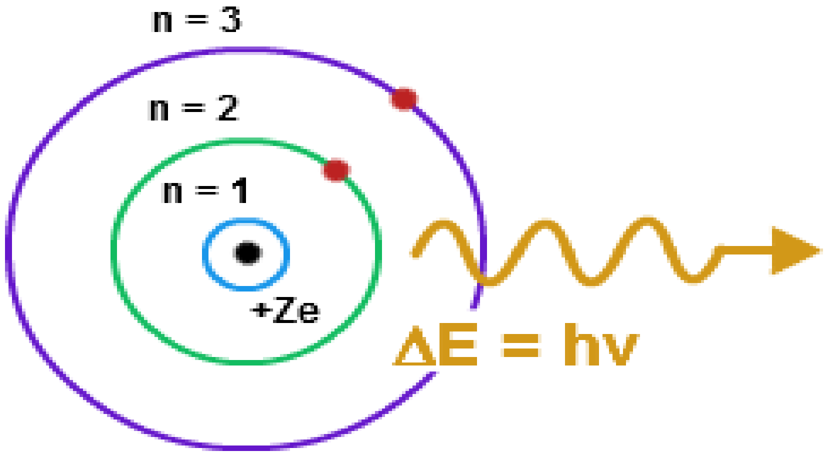
The energy of a photon emitted or absorbed is given by using **Planck's relation**

($E = h\nu$). If E_1be the energy of any lower energy state and E_2 be the energy of any higher energy state then the energy of the photon (emitted or absorbed) is given as ΔE:

$$\boxed{\Delta E = E_2 - E_1 = h\nu}$$

Where h = Planck's constant and **ν** = frequency of radiation emitted or absorbed.

Though the Bohr postulates of atomic model worked quite well it has certain limitations. It is applicable only to one electron atoms like helium He^+ and lithium Li^{++} apart from hydrogen H^- atom.



Here, we shall discuss the concept of Bohr’s orbits by defining the radius of orbits around the nucleus and the velocity and energy of an electron in various orbits around the nucleus.

We take the following assumptions:

r_n : radius of nth orbit

v_n : velocity of electron in nth state (orbit)

E_n : energy of nth state

m: mass of an electron (9.1 x 10^{-31} Kg)

Z: atomic number (No. of Protons)

$K = 1/(4\pi\varepsilon_0)$ = constant = 9 x 10^9 N m^2 C^{-2}

h: Planck's constant (6.67 x 10^{-34} Js)

c: velocity of light (3 x 10^8 m/s)

R: Rydberg constant (1.097 x 10^7 m^{-1})

e: Charge on an electron (1.6 x 10^{-19} C)

ν: frequency of the radiation emitted or absorbed

$\bar{\nu}$: wave number of the spectral line in the atomic spectra

From Bohr’s first postulate,

$mv^2 / r_n = KZe^2 / r_n^2$

From Bohr’s second postulate,

$mv_n r_n = nh / 2\pi$

Solving for r_n and v_n, we have:

Radius,

$= 0.53 \times 10^{-10}\ n^2/Z$ m

$= 0.53\ n^2 / Z$ A

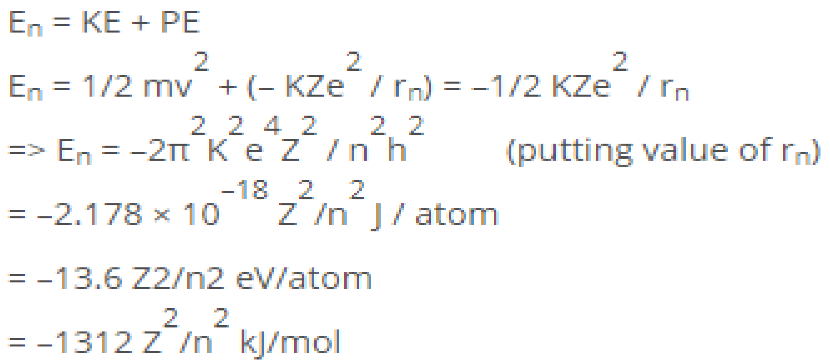
$$r_n = \frac{n^2 h^2}{4\pi^2 K m e^2 Z}$$

Velocity,

$= (2.165 \times 10^6\ Z/n)$ m/s

$$v_n = \frac{2\pi^2 K m e^2 Z}{nh}$$

Energy of an electron in ‘n’ th state E_n :-



E_n = KE + PE

$E_n = 1/2\ mv^2 + (-\ KZe^2\ /\ r_n) = -1/2\ KZe^2\ /\ r_n$

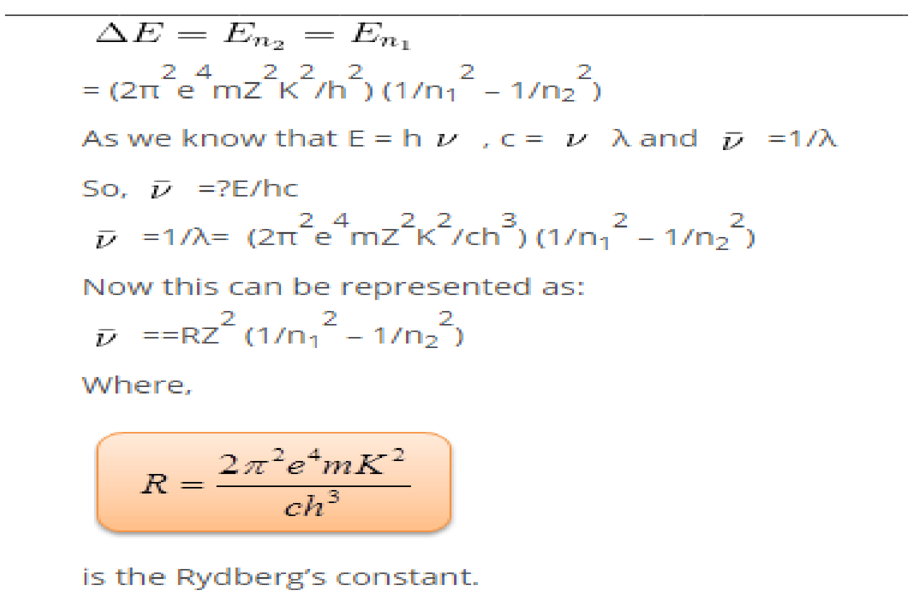
$\Rightarrow E_n = -2\pi^2 K^2 e^4 Z^2\ /\ n^2 h^2$ (putting value of r_n)

$= -2.178 \times 10^{-18}\ Z^2/n^2$ J / atom

$= -13.6\ Z2/n2$ eV/atom

$= -1312\ Z^2/n^2$ kJ/mol

When an electron jumps from an outer orbit (higher energy) n_2 to an inner orbit (lower energy) n_1, then the energy emitted in form of radiation is given by:



$$\Delta E = E_{n_2} = E_{n_1}$$

$= (2\pi^2 e^4 mZ^2 K^2/h^2)\ (1/n_1^2 - 1/n_2^2)$

As we know that $E = h\nu$, $c = \nu\lambda$ and $\bar{\nu} = 1/\lambda$

So, $\bar{\nu}$ =?E/hc

$\bar{\nu} = 1/\lambda = (2\pi^2 e^4 mZ^2 K^2/ch^3)\ (1/n_1^2 - 1/n_2^2)$

Now this can be represented as:

$\bar{\nu}$ ==$RZ^2\ (1/n_1^2 - 1/n_2^2)$

Where,

$$\boxed{R = \frac{2\pi^2 e^4 mK^2}{ch^3}}$$

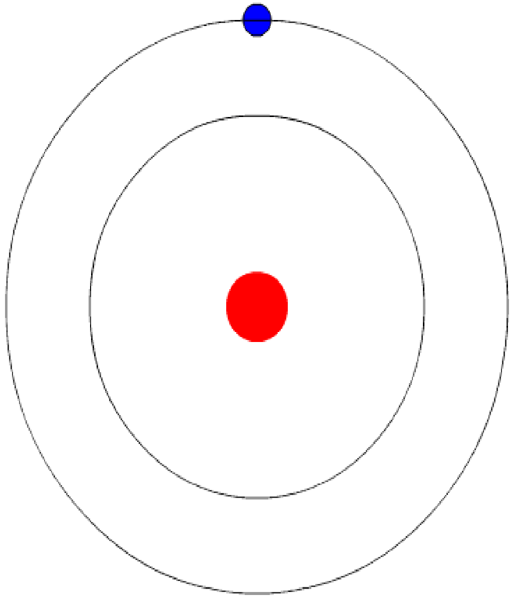
is the Rydberg’s constant.

Points to be noted:-

Bohr's Theory was quite successful as it introduced various new concepts about atom. The relation given by Bohr resembles the empirical relation given by Balmer& Rydberg on the spectral lines in H-atom spectra.

The value of R as obtained above in the Bohr's theory is the same as obtained in the empirical relation.

Bohr's atomic model postulates introduced various concepts like:



- ✓Bohr found that closer the electron to the nucleus the less energy it needs, while if it is far away from the nucleus it requires more energy. Because of this Bohr numbered the energy levels of electrons. If the energy level is high, farther is the electron from the nucleus.
- ✓He also found that there is a fixed number of electrons that every energy level can hold. The level 1 can hold up to 2 electrons, while the level 2 can hold up to 8 electrons and so on.

Limitations of the Bohr Model

- The Bohr Model was an important step in the development of atomic theory. However, it has several limitations.
- It is in violation of the Heisenberg Uncertainty Principle. The Bohr Model considers electrons to have both a known radius and orbit, which is impossible according to Heisenberg.
- The Bohr Model is very limited in terms of size. Poor spectral predictions are obtained when larger atoms are in question.
- It cannot predict the relative intensities of spectral lines.
- It does not explain the Zeeman Effect, when the spectral line is split into several components in the presence of a magnetic field.
- The Bohr Model does not account for the fact that accelerating electrons do not emit electromagnetic radiation.

Particle and wave nature of electron

In 1924 de Broglie equation states that a matter can act as waves much like light and radiation which also behave as waves and particles. The equation further explains that a beam of electrons can also be diffracted just like a beam of light. In essence, the de Broglie equation helps us understand the idea of matter having a wavelength.

Therefore, if we look at every moving particle whether it is microscopic or macroscopic it will have a wavelength.
In cases of macroscopic objects, the wave nature of matter can be detected or it is visible.

What is de Broglie Equation?

The de Broglie equation is one of the equations that is commonly used to define the wave properties of matter. It basically describes the wave nature of the electron.

Electromagnetic radiation, exhibit dual nature of a particle (having a momentum) and wave (expressed in frequency, wavelength). Microscopic particle-like electrons also proved to possess this dual nature property.

Louis de Broglie in his thesis suggested that any moving particle, whether microscopic or macroscopic will be associated with a wave character. It was called ‘Matter Waves’. He further proposed a relation between the velocity and momentum of a particle with the wavelength if the particle had to behave as a wave.

Particle and wave nature of matter, however, looked contradictory as it was not possible to prove the existence of both properties in any single experiment. This is because of the fact that every experiment is normally based on some principle and results related to the principle are only reflected in that experiment and not the other.

Nonetheless, both the properties are necessary to understand or describe the matter completely. Hence, particles and wave nature of matter are actually ‘complimentary’ to each other. It is not necessary for both to be present at the same time though. The significance of de Broglie relation is that it is more useful to microscopic, fundamental particles like electron.

de Broglie Equation Derivation and de Broglie Wavelength

Very low mass particles moving at speed less than that of light behaves like a particle and wave. De Broglie derived an expression relating the mass of such smaller particles and its wavelength.

Plank's Quantum theory relates the energy of an electromagnetic wave to its wavelength or frequency.

$$E = h\nu = \frac{hc}{\lambda} \quad \text{.......(1)}$$

Einstein related the energy of particle matter to its mass and velocity, as $E = mc^2$........(2)

As the smaller particle exhibits dual nature, and energy being the same, de Broglie equated both these relations for the particle moving with velocity 'v' as,

$$E = \, = \frac{hc}{\lambda} = mv^2 \; : \quad \text{Then, } \frac{h}{\lambda} = mv \text{ or } \lambda = \frac{h}{mv} = \frac{h}{\text{momentum}} \; : \text{ where 'h' is the Plank's constant.}$$

This equation relating the momentum of a particle with its wavelength is de Broglie equation and the wavelength calculated using this relation is de Broglie wavelength.

Relation Between de Broglie Equation and Bohr’s Hypothesis of Atom

Bohr postulated that angular momentum of an electron revolving around the nucleus as quantized. Hence, the angular momentum will only be an integral multiple of a constant value and suggested the following expression.

Angular momentum of electron in orbit = mvr $= \frac{nh}{2\pi}$: where ‘n’ is an integer with values of 1,2,3..

Bohr did not give any reason for such a proposal.

But, de Broglie equation gives a scientific validation for such an imaginative proposal.

The

By, de Broglie, equation $\lambda = \frac{h}{mv}$ or $mv = \frac{h}{\lambda}$

so,

Circumference of an orbit = integral multiple of the wavelength.

$2\pi r = n\lambda$ or $\frac{1}{\lambda} = \frac{n}{2\pi r}$

Substituting for wave length, in the De Broglie equation, $mv = \frac{nh}{2\pi r}$ or $mvr = n \times \frac{h}{2\pi}$

Hence the angular momentum of electron (mvr) is an integral multiple of a constant $\left(\frac{h}{2\pi}\right)$

1. Does, de Broglie hypothesis has any relevance to macroscopic matter?

Solution

de Broglie relation can be applied to both microscopic and macroscopic. Taking for example a macro sized 100Kg car moving at a speed of 100m/s, will have a-

$$\text{Wavelength of } \lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}}{100\times100} = 6.63 \times 10^{-30} m$$

High-energy γ-radiations have wavelength of only 10^{-12} m.

Very small wavelength corresponds to high frequencies. Waves below certain wavelength or beyond certain frequencies undergo particle-antiparticle annihilation to create mass. So, wave nature or de Broglie wavelength is not observable in the macroscopic matter.

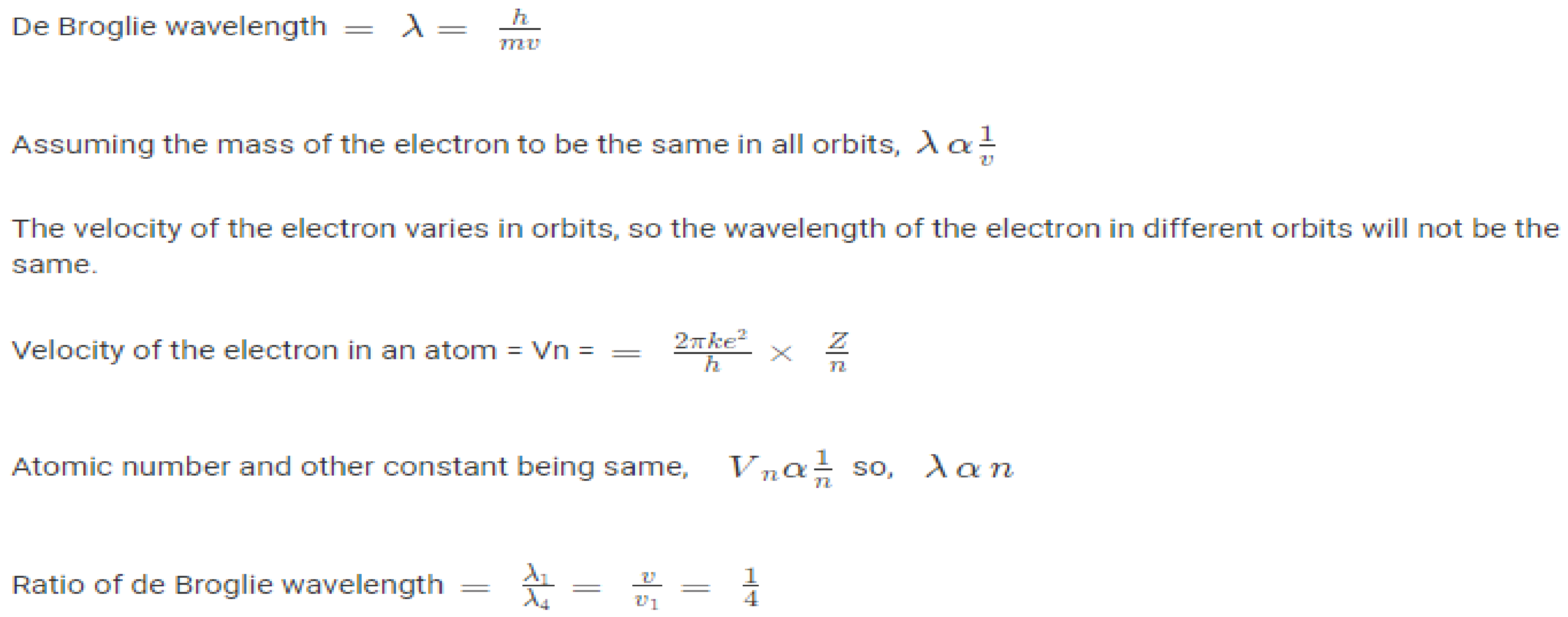
2. Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other types of material. If the velocity of the electron in this microscope is 1.6 × $10^6 ms^{-1}$, calculate de Broglie wavelength associated with this electron.

Solution

de Broglie Wavelength of $\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}}{9.1\times10^{-31}\,1.6\times10^{6}} = 4.55\times\ 10^{-10}m$

3. Is the wavelength of electron on different orbits, same or different? If different what is the ratio of the wavelength in first and 4th orbit?

Solution



De Broglie wavelength $= \lambda = \frac{h}{mv}$

Assuming the mass of the electron to be the same in all orbits, $\lambda \alpha \frac{1}{v}$

The velocity of the electron varies in orbits, so the wavelength of the electron in different orbits will not be the same.

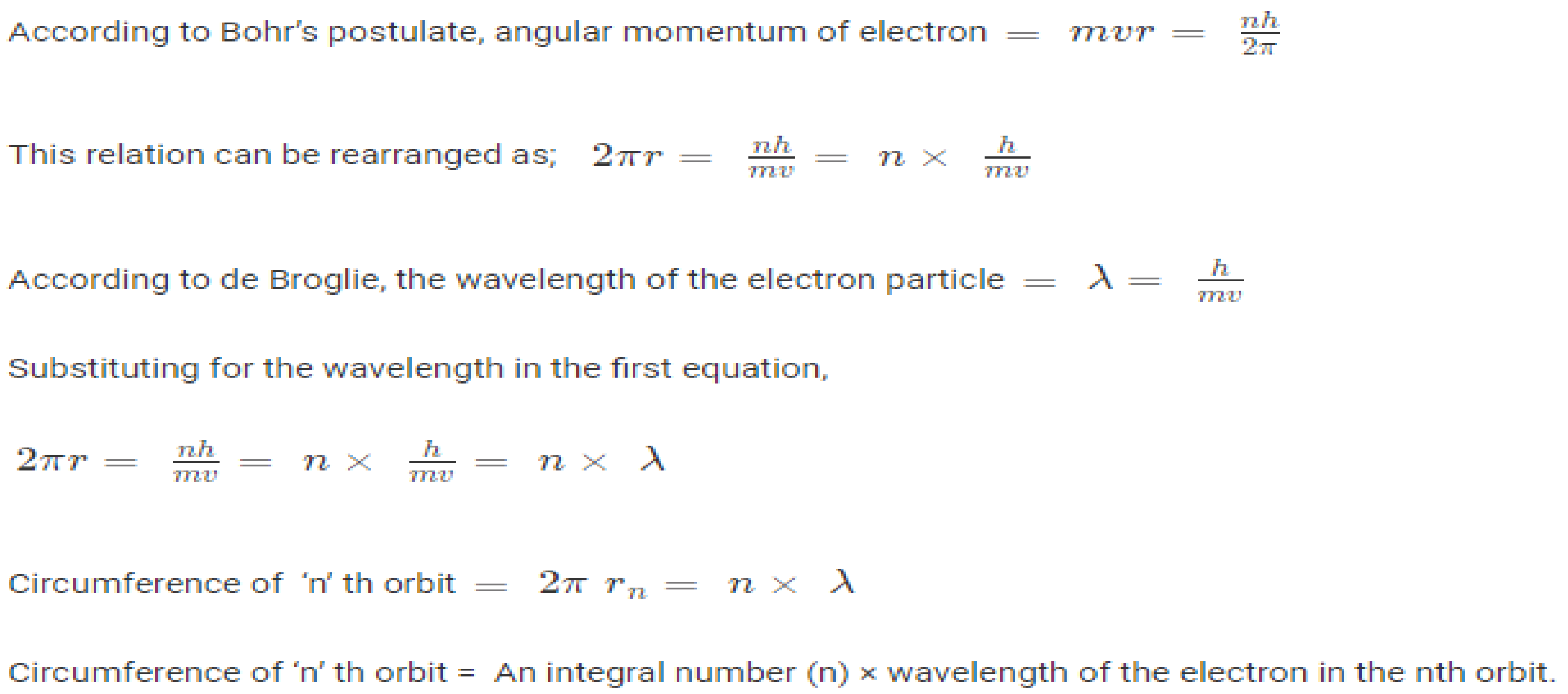
Velocity of the electron in an atom = Vn = $= \frac{2\pi ke^2}{h} \times \frac{Z}{n}$

Atomic number and other constant being same, $V_n \alpha \frac{1}{n}$ so, $\lambda \alpha n$

Ratio of de Broglie wavelength $= \frac{\lambda_1}{\lambda_4} = \frac{v}{v_1} = \frac{1}{4}$

4. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit.

Solution



According to Bohr's postulate, angular momentum of electron $= mvr = \frac{nh}{2\pi}$

This relation can be rearranged as; $2\pi r = \frac{nh}{mv} = n \times \frac{h}{mv}$

According to de Broglie, the wavelength of the electron particle $= \lambda = \frac{h}{mv}$

Substituting for the wavelength in the first equation,

$$2\pi r = \frac{nh}{mv} = n \times \frac{h}{mv} = n \times \lambda$$

Circumference of 'n' th orbit $= 2\pi\ r_n = n \times \lambda$

Circumference of 'n' th orbit = An integral number (n) × wavelength of the electron in the nth orbit.

Heisenberg Uncertainty Principle

Heisenberg uncertainty principle imposes a restriction on the accuracy of simultaneous measurement of position and momentum. The more precise our measurement of position is, the less accurate will be our momentum measurement and vice-versa.

The physical origin of the Heisenberg uncertainty principle is with the quantum system. Determination of position by performing measurement on the system disturbs it sufficiently to make the determination of q imprecise and vice-versa.

Heisenberg uncertainty principle states that for particles with the dual nature of particle and wave nature, it will not be possible to accurately determine both the position and velocity at the same time. The principle is named after German physicist, Werner Heisenberg who proposed the uncertainty principle in the year 1927. This principle was formulated when Heisenberg was in trying to build an intuitive model of quantum physics. He discovered that there were certain fundamental factors that limited our actions in knowing certain quantities.

This principle basically highlights that simultaneous measurement of position and the velocity or momentum of microscopic matter waves will have an error such that the product of the error in measurement of position and momentum is equal or more than an integral multiple of a constant.

Heisenberg Uncertainty Principle Formula and Application

If, Δx is the error in position measurement and Δp is the error in the measurement of momentum, then

$$\Delta X \times \Delta p \geq \frac{h}{4\pi}$$

Since momentum, p = mv, Heisenberg's uncertainty principle formula can be alternatively written as-

$$\Delta X \times \Delta mv \geq \frac{h}{4\pi} \text{ or } \Delta X \times \Delta m \times \Delta v \geq \frac{h}{4\pi}$$

Where, ΔV is the error in the measurement of velocity and assuming mass remaining constant during the experiment, $\Delta X \times \Delta V \geq \frac{h}{4\pi m}$.

Accurate measurement of position or momentum automatically indicates larger uncertainty (error) in the measurement of the other quantity.

Applying the Heisenberg principle to an electron in an orbit of an atom, with $h = 6.626 \times 10^{-34}$Js and $m= 9.11 \times 10^{-31}$Kg, $\Delta X \times \Delta V \geq \frac{6.626\times10^{-34}}{4\times3.14\times9.11\times10^{-31}} = 10^{-4}\, m^2\, s^{-1}$.

If the position of the electron is measured accurately to its size (10^{-10}m), then the error in the measurement of its velocity will be equal or larger than 10^{6}m or 1000Km.

Heisenberg principle applies to only dual-natured microscopic particles and not to a macroscopic particle whose wave nature is very small.

Explaining Heisenberg Uncertainty Principle With An Example

Electromagnetic radiations and microscopic matter waves exhibit a dual nature of mass/ momentum and wave character. Position and velocity/momentum of macroscopic matter waves can be determined accurately, simultaneously. For example, the location and speed of a moving car can be determined at the same time, with minimum error. But, in microscopic particles, it will not be possible to fix the position and measure the velocity/momentum of the particle simultaneously.

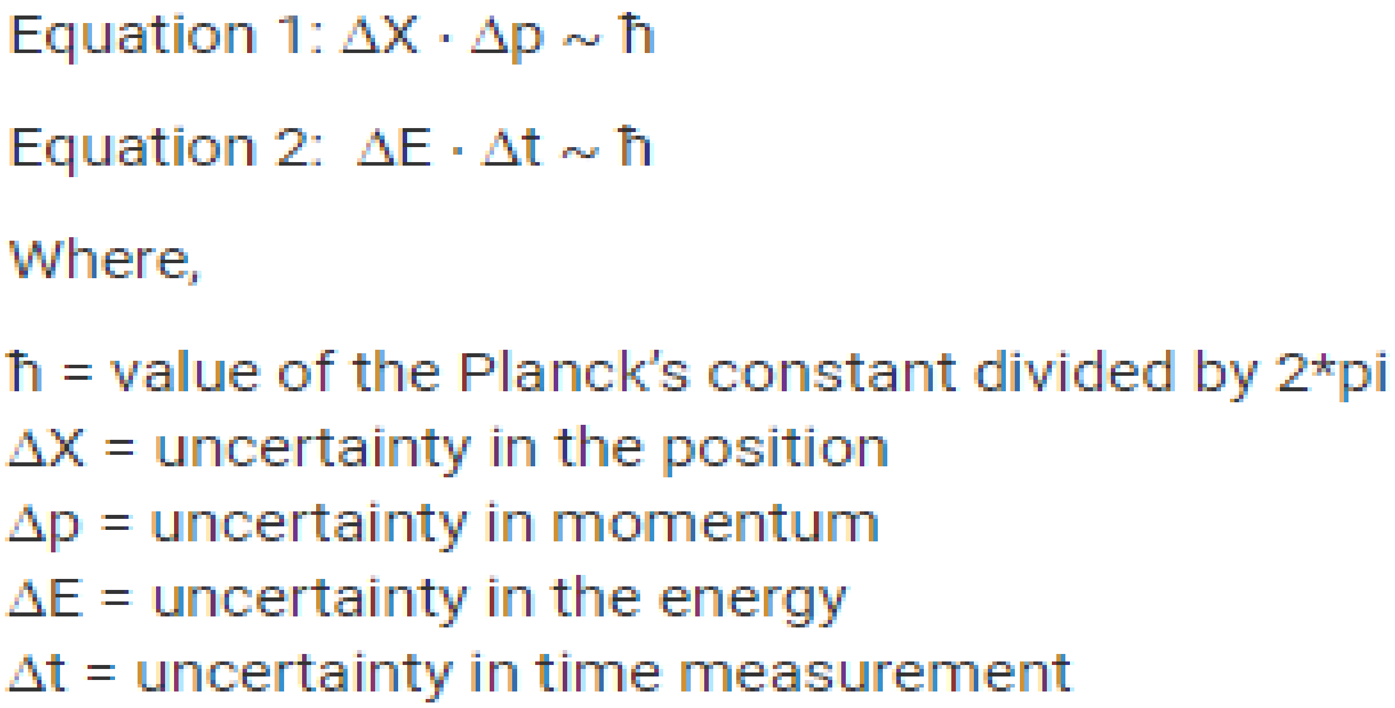
An electron in an atom has a mass of 9.91×10^{-31}Kg. Naked eyes will not see such small particles. A powerful light may collide with the electron and illuminate it. Illumination helps in identifying and measuring the position of the electron. The collision of the powerful light source, while helping in identification increases the momentum of the electron and makes it move away from the initial position. Thus, when fixing the position, velocity /momentum of the particle would have changed from the original value. Hence when the position is exact, error occurs in the measurement of velocity or momentum. In the same way, the measurement of momentum accurately will change the position.

Hence, at any point in time, either position or momentum can only be measured accurately.

Simultaneous measurement of both of them will have an error in both position and momentum. Heisenberg quantified the error in the measurement of both position and momentum at the same time.

Heisenberg Uncertainty Principle Equations

Heisenberg’s uncertainty principle can be considered as a very precise mathematical statement that describes the nature of quantum systems. As such, we often consider two common equations related to the uncertainty principle. They are;



Equation 1: $\Delta X \cdot \Delta p \sim \hbar$

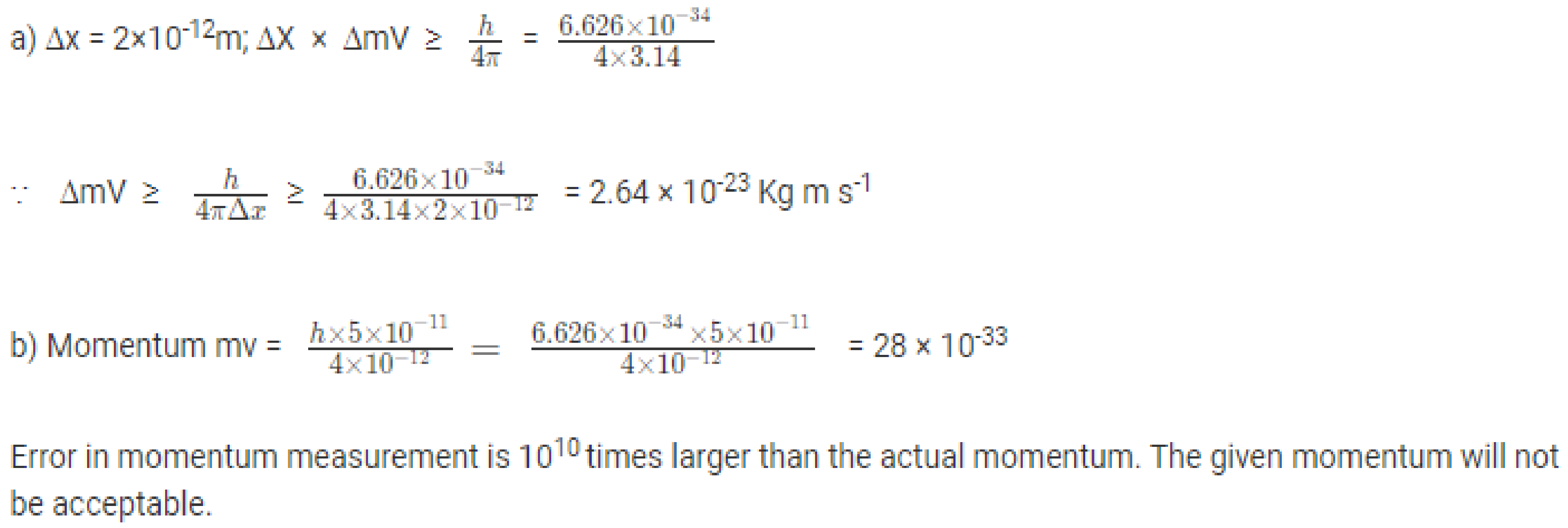
Equation 2: $\Delta E \cdot \Delta t \sim \hbar$

Where,

$\hbar$ = value of the Planck's constant divided by 2*pi
ΔX = uncertainty in the position
Δp = uncertainty in momentum
ΔE = uncertainty in the energy
Δt = uncertainty in time measurement

1. If the position of the electron is measured within an accuracy of + 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is *h* / 4p*m* × 0.05 nm, is there any problem in defining this value.

Solution



a) $\Delta x = 2\times10^{-12}$m; $\Delta X \times \Delta mV \geq \frac{h}{4\pi} = \frac{6.626\times10^{-34}}{4\times3.14}$

$\because \Delta mV \geq \frac{h}{4\pi\Delta x} \geq \frac{6.626\times10^{-34}}{4\times3.14\times2\times10^{-12}} = 2.64\times10^{-23}$ Kg m s^{-1}

b) Momentum mv = $\frac{h\times5\times10^{-11}}{4\times10^{-12}} = \frac{6.626\times10^{-34}\times5\times10^{-11}}{4\times10^{-12}} = 28\times10^{-33}$

Error in momentum measurement is 10^{10} times larger than the actual momentum. The given momentum will not be acceptable.

2. Position of a chloride ion on a material can be determined to a maximum error of 1µm. If the mass of the chloride ion is 5.86×10^{-26}Kg, what will be the error in its velocity measurement?

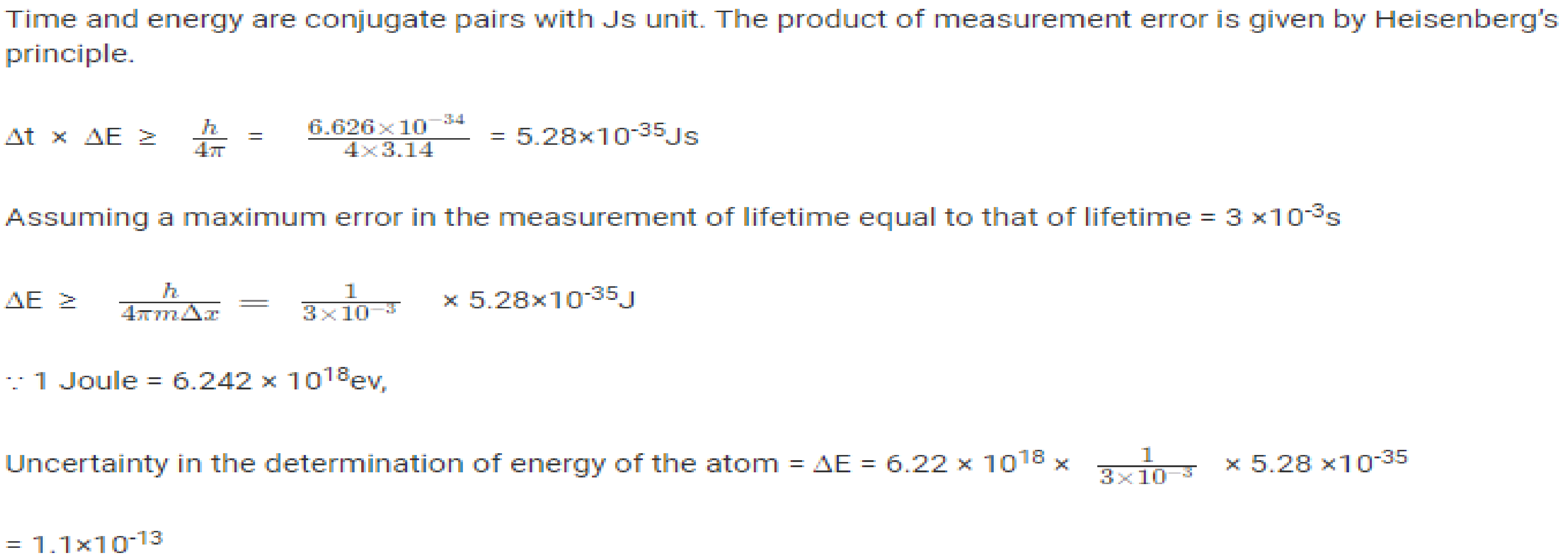
Solution

$$\Delta x = 10^{-6}\,\text{m};\ \Delta X \times \Delta mV \geq \frac{h}{4\pi} = \frac{6.626\times10^{-34}}{4\times3.14} = 5.28\times10^{-35}\,\text{Js}$$

$$\because\ \Delta V \geq \frac{h}{4\pi m\Delta x} \geq \frac{6.626\times10^{-34}}{4\times3.14\times5.86\times10^{-26}\times10^{-6}} = 9\times10^{-4}\,\text{m s}^{-1}$$

3. The lifetime of an excited state of an atom is 3×10^{-3}s. What is the minimum uncertainty in its energy in eV?

Solution



Time and energy are conjugate pairs with Js unit. The product of measurement error is given by Heisenberg's principle.

$\Delta t \times \Delta E \geq \frac{h}{4\pi} = \frac{6.626 \times 10^{-34}}{4 \times 3.14} = 5.28 \times 10^{-35}$ Js

Assuming a maximum error in the measurement of lifetime equal to that of lifetime = 3×10^{-3}s

$\Delta E \geq \frac{h}{4\pi m \Delta x} = \frac{1}{3 \times 10^{-3}} \times 5.28 \times 10^{-35}$ J

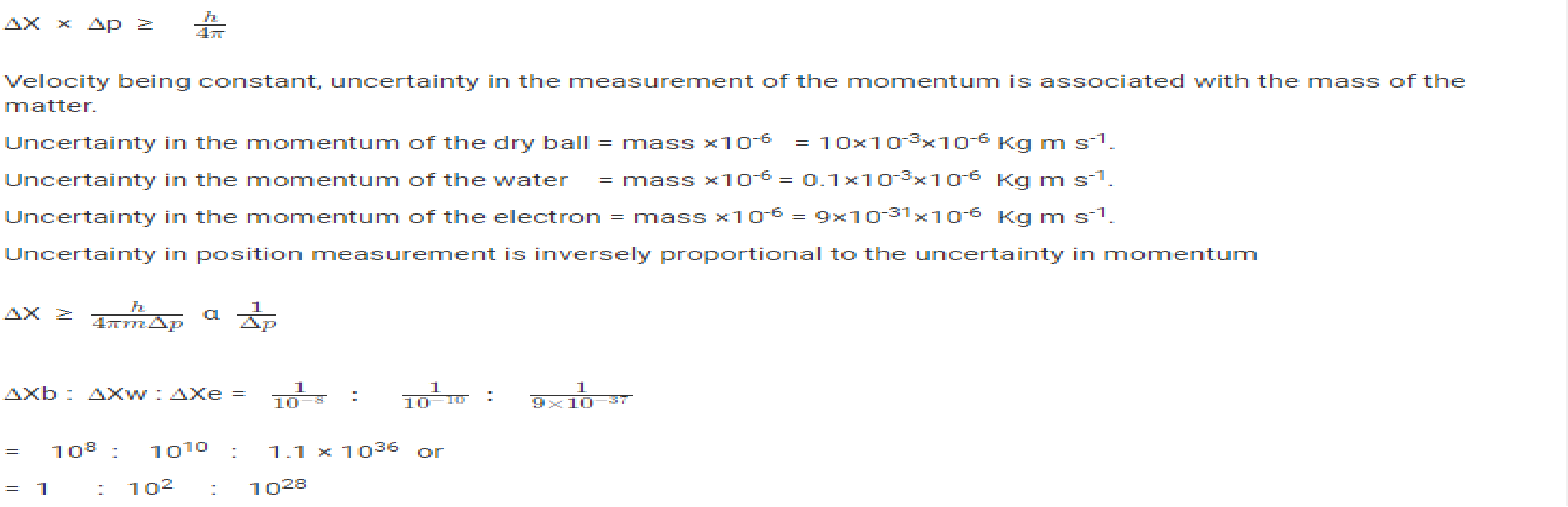
$\because$ 1 Joule = 6.242×10^{18}ev,

Uncertainty in the determination of energy of the atom = $\Delta E = 6.22 \times 10^{18} \times \frac{1}{3 \times 10^{-3}} \times 5.28 \times 10^{-35}$

$= 1.1 \times 10^{-13}$

4. A wet ball weighing 10.1gm has a water of 0.1g on it. The ball is moving with a constant velocity with an uncertainty of momentum of 10^{-6} kg m/s. What will be the uncertainty in the measurement of the position of the ball, water and electron in the water molecule?

Solution



$\Delta X \times \Delta p \geq \frac{h}{4\pi}$

Velocity being constant, uncertainty in the measurement of the momentum is associated with the mass of the matter.

Uncertainty in the momentum of the dry ball = mass $\times 10^{-6}$ = $10\times10^{-3}\times10^{-6}$ Kg m s^{-1}.

Uncertainty in the momentum of the water = mass $\times 10^{-6}$ = $0.1\times10^{-3}\times10^{-6}$ Kg m s^{-1}.

Uncertainty in the momentum of the electron = mass $\times 10^{-6}$ = $9\times10^{-31}\times10^{-6}$ Kg m s^{-1}.

Uncertainty in position measurement is inversely proportional to the uncertainty in momentum

$\Delta X \geq \frac{h}{4\pi m \Delta p} \ \alpha \ \frac{1}{\Delta p}$

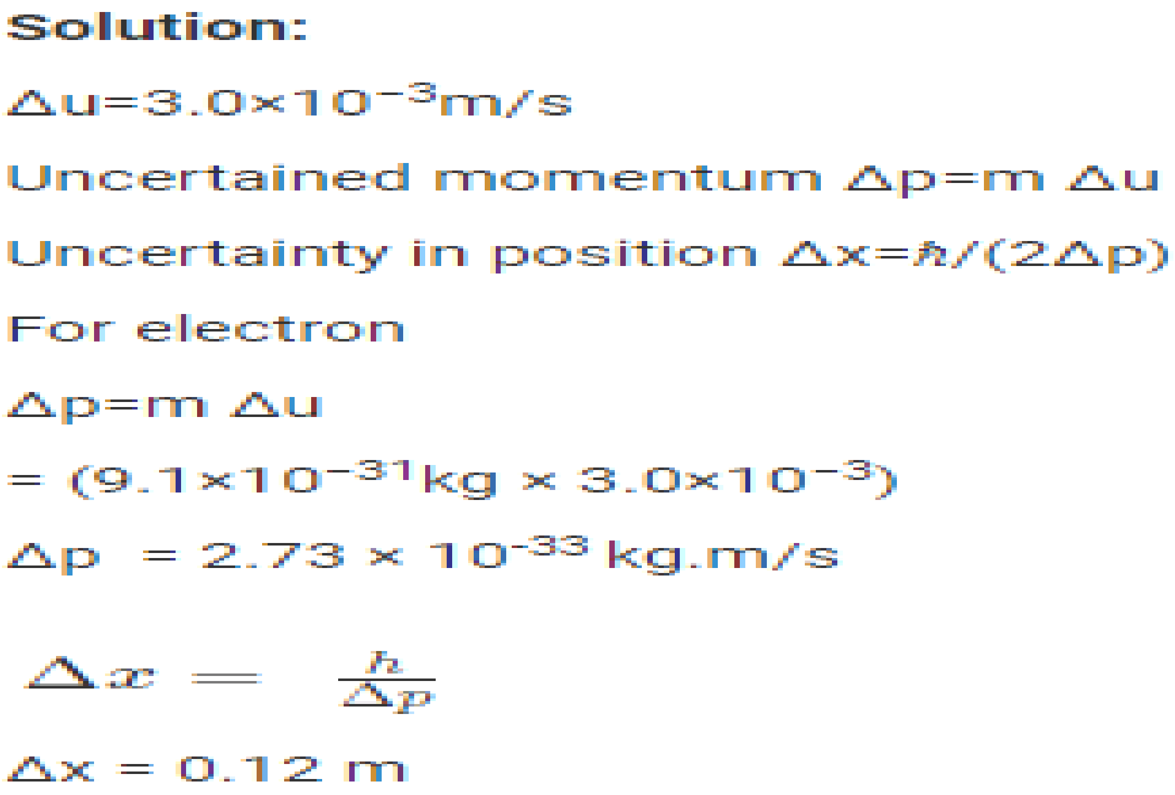
$\Delta Xb : \Delta Xw : \Delta Xe = \frac{1}{10^{-8}} : \frac{1}{10^{-10}} : \frac{1}{9\times10^{-37}}$

$= 10^{8} : 10^{10} : 1.1 \times 10^{36}$ or

$= 1 : 10^{2} : 10^{28}$

5. Determine the minimum uncertainties in the positions of the electron if their speeds are known with a precision of 3.0×10^{-3}m/s?

Solution



Solution:

$\Delta u = 3.0 \times 10^{-3}$ m/s

Uncertained momentum $\Delta p = m\ \Delta u$

Uncertainty in position $\Delta x = \hbar/(2\Delta p)$

For electron

$\Delta p = m\ \Delta u$

$= (9.1 \times 10^{-31}\text{kg} \times 3.0 \times 10^{-3})$

$\Delta p = 2.73 \times 10^{-33}$ kg.m/s

$$\Delta x = \frac{h}{\Delta p}$$

$\Delta x = 0.12$ m

Quantum Mechanical Model of Atom

- Quantum mechanics is based on Schrödinger’s wave equation and its solution. The solution of the wave equation brings the idea of shells, sub-shells and orbitals. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point, where ψ represents the wave-function of that electron.
- Application of Schrödinger’s equation to multi-electron atoms present’s some difficulty: Schrödinger’s wave equation cannot be solved exactly for a multi-electron atom. This difficulty was overcome by using approximate methods.
- The application of Schrödinger wave equation in determining the structure of ab atom led to the formation of the quantum mechanical model of an atom.

Features of quantum mechanical model:

- The energy of an electron is quantized i.e. an electron can only have certain specific values of energy.
- The quantized energy of an electron is the allowed solution of the Schrödinger wave equation and it is the result of wave like properties of electron.
- As per Heisenberg's Uncertainty principle, the exact position and momentum of an electron cannot be determined. So the only probability of finding an electron at a position can be determined and it is $|\psi|^2$ at that point where ψ represents the wave-function of that electron.
- An atomic orbital is the wave-function (ψ) of an electron in an atom. Whenever an electron is described by a wave-function, it occupies atomic orbital. As an electron can have many wave-functions, there are many atomic orbitals for electron. Every wave-function or atomic orbital have some shape and energy associated with it. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.
- The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as probability density and is always positive.

Orbitals

Orbitals in Physics and Chemistry is a mathematical function depicting the wave nature of an electron or a pair of electrons present in an atom. The probability of finding an electron around the nucleus can be calculated using this function. In simpler terms, atomic orbital can be described as the physical bounded region or space where the electrons are present. Generally, an atom consists of electrons that are fixed inside the electronic orbitals.

Atomic Orbitals and Quantum Numbers

If we look at any atomic orbital, it is generally associated with three quantum numbers. That being said, Schrodinger's equation solution also provides the possible energy levels that electrons can occupy and the associated wave function(s) (ψ) corresponding to each energy level. Each quantized energy states are characterized by a set of three quantum numbers n, ℓ, and ml depicting the energy, angular momentum, shape.

An atomic orbital is known as the wave function ψ for an electron in an atom. Nonetheless, the quantum numbers help us to clearly describe the arrangement of the electrons in a particular atom.

1. The principal quantum number 'n' is a positive integer having the values **1,2,3……**The principal quantum number tells the size and energy of the orbital. All the orbitals of 'n' contains a single shell of an atom.

2. Azimuthal quantum number 'l' is referred to as subsidiary quantum number or orbital angular momentum number and defines an orbital's three-dimensional shape.

Each shell constitutes one or more than one subshells or sub-levels. The number of subshells in a principal shell is equal to the value of n.

Different value for **l : 0 1 2 3 4** corresponds to **s p d f g** orbitals respectively.

3. Magnetic orbital quantum number 'm' describes an orbital's spatial orientation in accordance with the co-ordinate axis.

4. Spin quantum number 's' is a spin angular momentum of the electron. There are two orientations which describe the spin values **+½ or –½.** These are known as the two spin states for an electron.

Meanwhile, the size, as well as the shape of orbitals, is usually determined from the square of the wave function Ψ^2.

Types of Orbitals

s orbital

S orbital is spherically symmetrical orbital around the atomic nucleus. The energy level increases as we move away from the nucleus, therefore the orbitals get bigger. The order of size is 1s< 2s< 3s<.

The probability of finding an electron is maximum in 1s and decreases rapidly as we move away from it. In the case of 2s orbital, the probability density decreases sharply to zero and again starts increasing. On reaching a small maximum it decreases again and finally reaches to zero if the value of r increases further.

The nodal point is a point at which there is a zero probability of finding the electron. There are two types of nodes: Radial nodes and angular nodes. The radial nodes calculate the distance from the nucleus while the angular node determines direction.

- No. of radial nodes = $n - l - 1$
- No. of angular nodes = l
- Total number of nodes = $n - 1$

Nodal planes are defined as the planes of zero probability region to find the electron. The number of planes is equal to l.

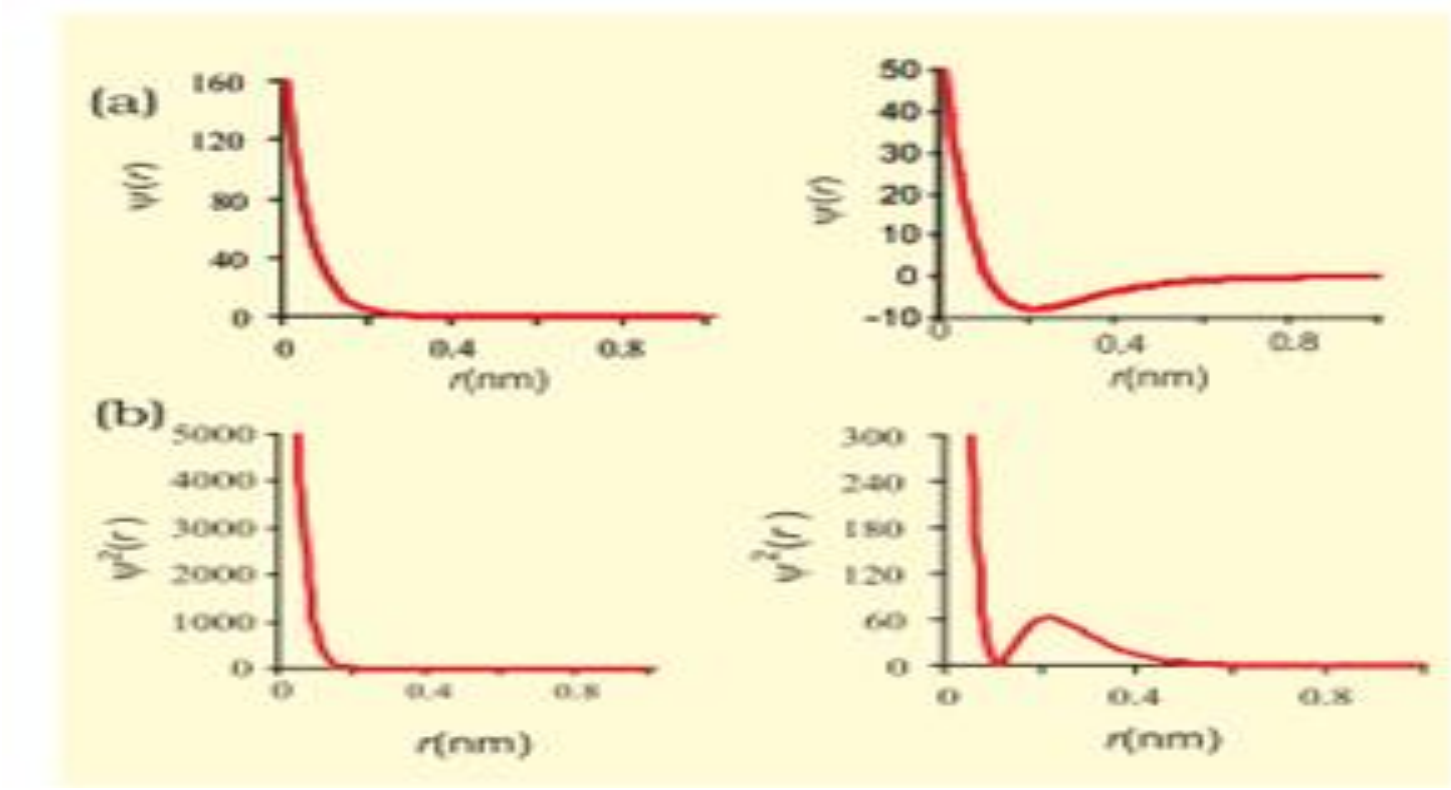


Figure : The plots of (a) the orbital wave function $\psi(r)$; (b) the variation of probability density ψ^2 (r) as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.

Boundary surface diagrams of the constant probability density for different atomic orbitals provides a good representation of the shapes of the atomic orbitals. In the figure, a boundary surface or contour surface is drawn in space for the orbital where the value of probability density $|\psi|^2$ is constant. The 1s and 2s orbital are spherical in shape but the s orbitals are in general spherical symmetric. This means that the probability of finding the electron at a given distance is equally uniform in all directions.

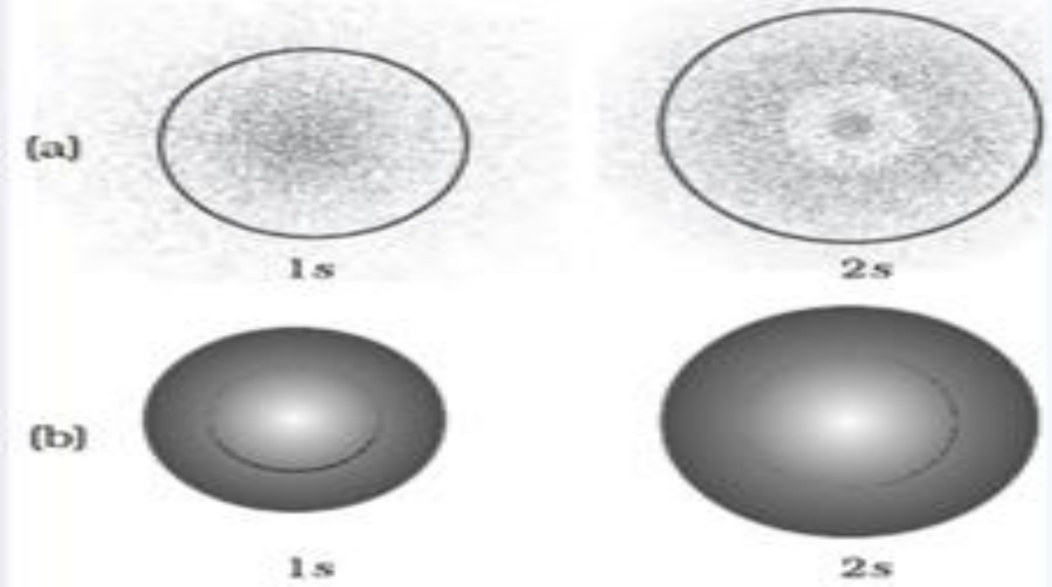


Figure : (a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface representation for 1s and 2s orbitals.

p Orbital

The p orbitals are dumbbell-shaped. The node in the p orbital occurs at the centre of the nucleus. The p orbital can occupy a maximum of six electrons due to the presence of three orbitals. The three p orbitals are oriented right angles to each other. The size of the p orbitals depends on the principal quantum number n i.e; 4p > 3p > 2p.

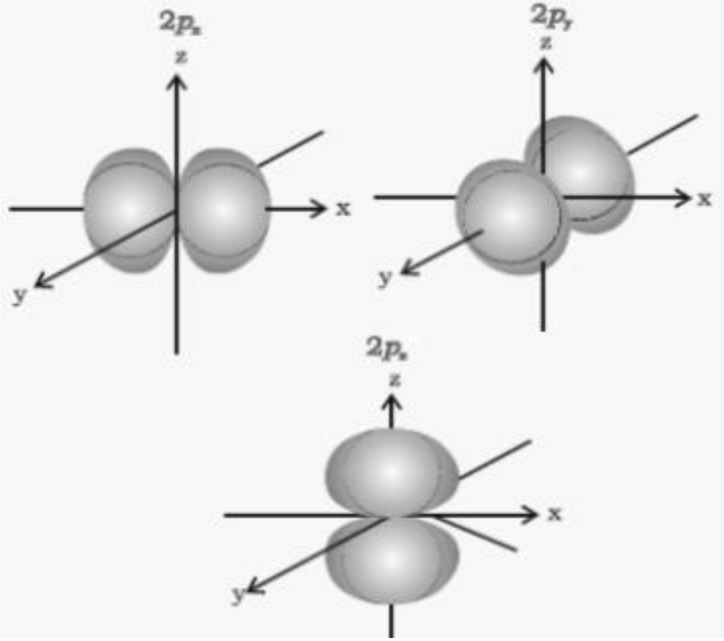


Figure : Boundary surface diagrams of the three 2p orbitals.

Each p orbital has sections known as lobes which are present on either side of the plane which passes through the nucleus. The probability of finding an electron is zero at the plane where the two lobes intersect each other. The three orbital has identical size, shape and energy so-termed as degenerate orbitals. The orbitals only differ in the orientation of the lobes. The lobes are oriented along the x, y or z-axis thus are assigned with the designations 2px, 2py, and 2pz. The number of nodes is calculated by the formula n –2.

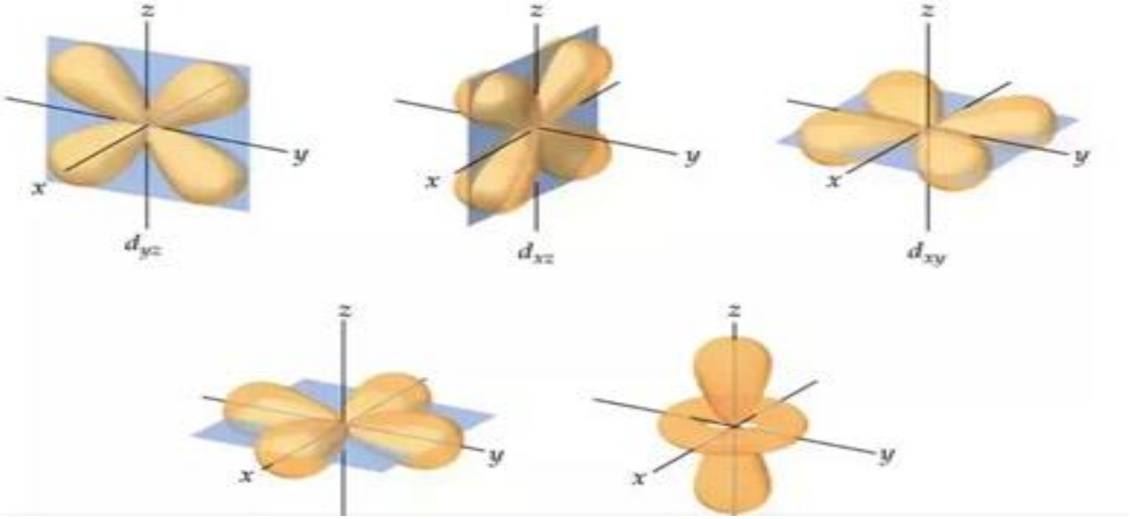
Orbital	p_x	p_y	p_z
m	-1 or +1	+1 or -1	0
Nodal plane	xy	yz	xz

d orbital

The d orbital is cloverleaf or two dumbbells in a plane. For d orbital the value of l=2 thus the minimum value of principal quantum number n is 3. The value for l cannot be greater than n-1. The values of ml corresponding to d orbital are (–2, –1, 0, +1 and +2) for l = 2 therefore, there are five d orbitals.

The five d-orbitals are assigned with the designation dxy, dyz, dxz, dx^{2}–y^{2} and dz^{2}. The energy of all five orbitals are equal but the first four orbitals are similar in shape to each other while the dz^{2} differ from others. The radical node (probability density function) is zero. The d$_{xy}$ orbital has two nodal planes passing through the origin and bisects the xy plane consisting z-axis. There are two angular nodes for d orbital.

Figure : Boundary surface diagrams of the five d orbitals**.**



Orbital	**Nodal planes**
d_{xy}	xz, yz
d_{yz}	xy, zx
d_{zx}	xy, yz
$d_{x^2-y^2}$	x-y=0, x+y=0
d_{z^2}	No nodal plane

f Orbitals

f orbital has diffused shape. For f orbital the value of l=3 thus the minimum value of principal quantum number n is 4. The values of ml corresponding to f orbital are (-3,–2, –1, 0, +1, +2, +3). For l = 3 therefore, there are seven f orbitals.

The seven orbitals are $f_{x(x^2-y^2)}$, $f_{y(x^2-y^2)}$, f_{xyz}, f_{z^3}, f_{yz}, f_{xz^2}, $f_{z(x^2-y^2)}$

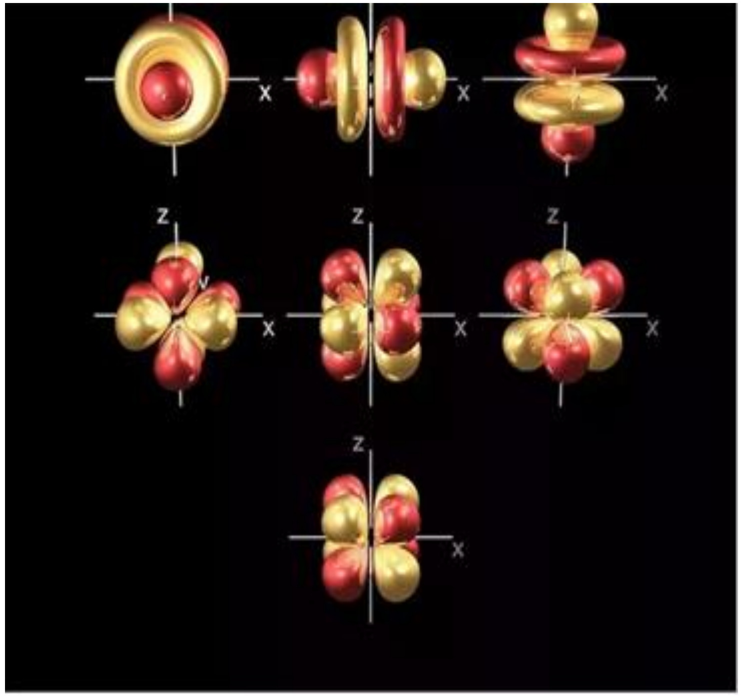


Figure : Boundary surface diagrams of the seven f orbitals.

Degenerate Orbitals

Degenerate orbitals are orbitals having the same energy. These orbital are different (may have a different orientation in space around the atomic nucleus) but possess the same energy. The degeneracy of p orbital remains unaffected in presence of external field but degeneracy of f and d orbital can be broken by applying an external field to the system (either electric or magnetic field).

Few orbitals will possess higher energy and other lower energy. The system will no longer have degeneracy. For example, d orbitals consist of five degenerated orbitals and all five orbitals have exactly the same energy.

$P_x, p_y, p_z \rightarrow$ 3 fold degenerate

D orbitals → 5 fold degenerate

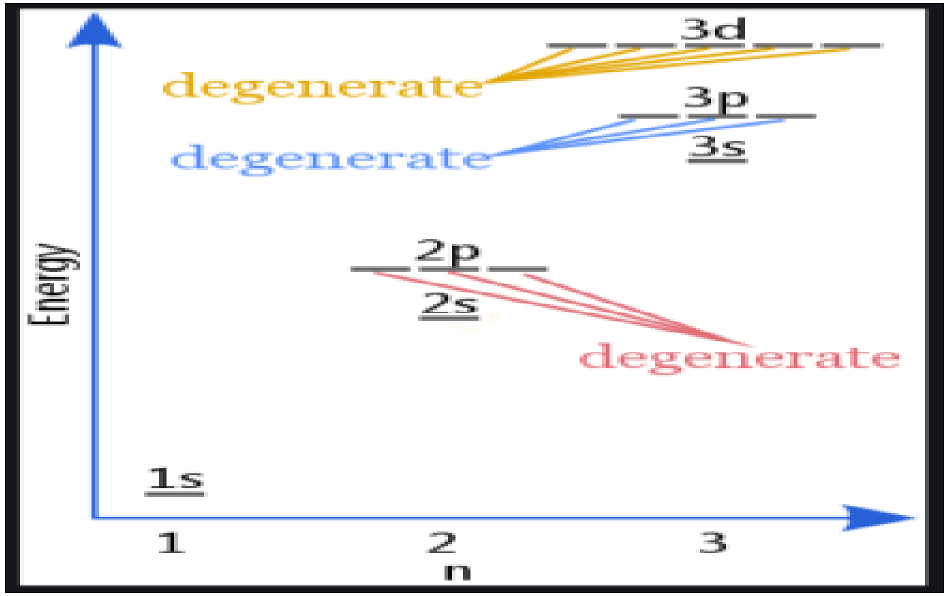


Figure : Degenerate orbitals

1. Calculate the degeneracy of the level of the hydrogen atom having energy – RH / 25.

Solution

The energy in H-atom, RH / n^2

On comparing the energy, the value of $n^2 = 25$

$n = 5$

The value of the azimuthal quantum number (l) is n-1

So the corresponding value of m is -l to +l

m=0, m=-1,0,1, m=-2,-1,0,1,2, m=-3,-2,-1,0,1,2,3, m=-4,-3,-2,-1,0,1,2,3,4

So the total number of orbitals are 1+3+4+7+9=25

The degeneracy of the energy levels of the hydrogen atom is 25.

2. Calculate the total spin resulting from a $3p^4$ configuration.

Solution

The total number of unpaired electrons in $3p^4$ is 2

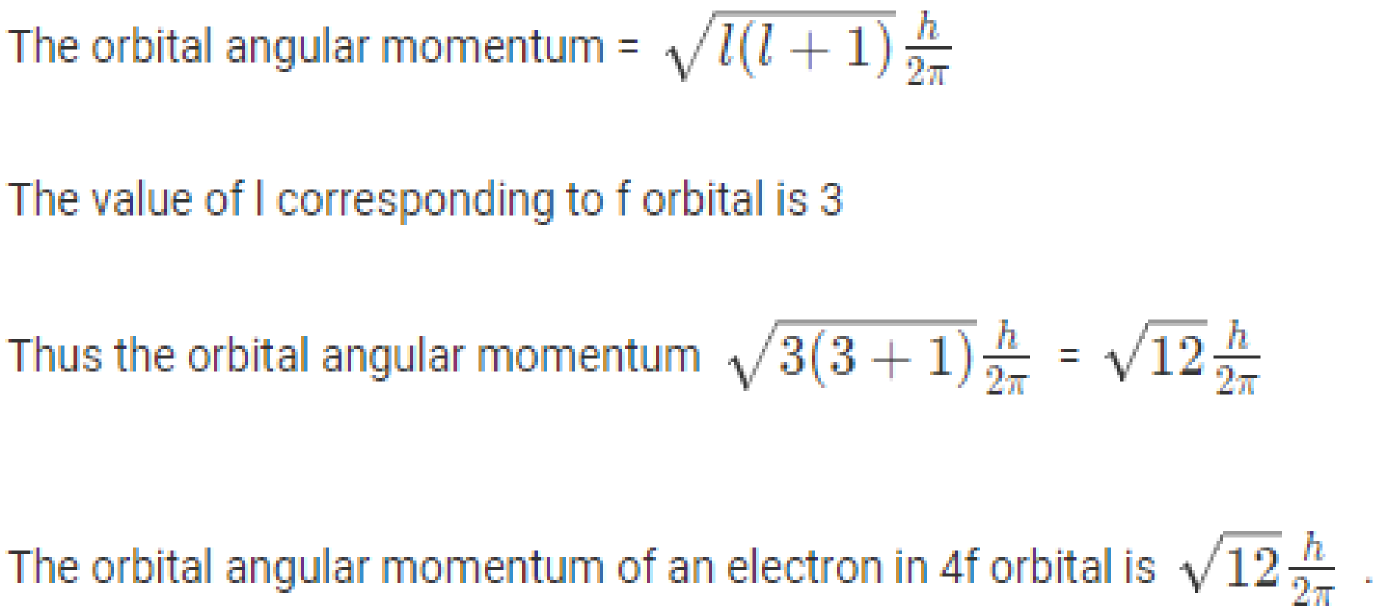
The total spin value is given by

Here, n is the number of unpaired electrons

The total spin resulting in $3p^4$ is 1.

3. Determine the orbital angular momentum of an electron in 4f orbital.

Solution



The orbital angular momentum = $\sqrt{l(l+1)}\frac{h}{2\pi}$

The value of l corresponding to f orbital is 3

Thus the orbital angular momentum $\sqrt{3(3+1)}\frac{h}{2\pi}$ = $\sqrt{12}\frac{h}{2\pi}$

The orbital angular momentum of an electron in 4f orbital is $\sqrt{12}\frac{h}{2\pi}$.

4. If the value of magnetic quantum number m for an electron in an atom is equal to the number of m values for l =1. In which orbital the electron is present?

Solution

The total values of m= (2l+1)

For l=1, the value of m is 21+1=3

m=3 for f subshell

So the electron is present in the f subshell.

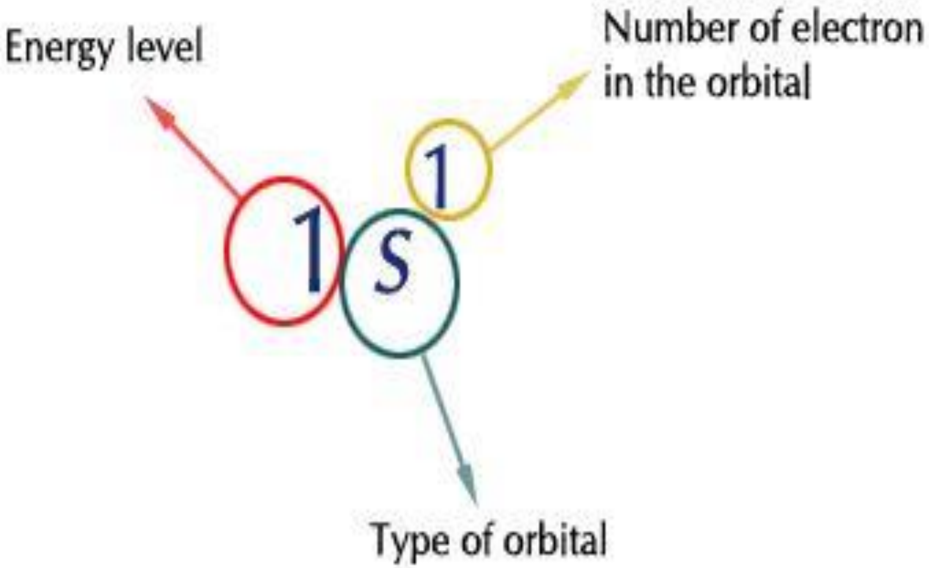
5. Which of the orbital has the shape of a baby-soother? And why?

Solution

The dz^2 orbital has the shape of a baby-soother because the orbital contains two lobes oriented in z-axis with the ring of high electron density concentrated in the xy plane. It contains no nodal plane rather has 2 nodal cones.

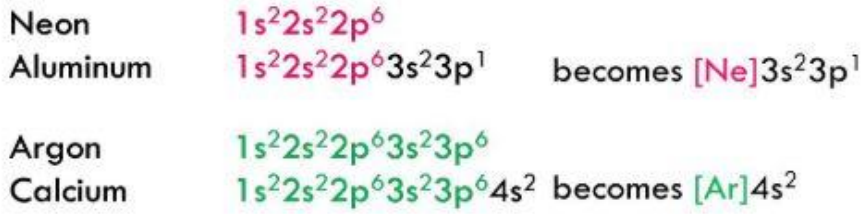
Electron Configurations

The electron configuration of an element describes how electrons are distributed in its atomic orbitals. Electron configurations of atoms follow a standard notation in which all electron-containing atomic subshells (with the number of electrons they hold written in superscript) are placed in a sequence. For example, the electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$.



However, the standard notation often yields lengthy electron configurations (especially for elements having a relatively large atomic number). In such cases, an abbreviated or condensed notation may be used instead of the standard notation.

In the abbreviated notation, the sequence of completely filled subshells that correspond to the electronic configuration of a noble gas is replaced with the symbol of that noble gas in square brackets. Therefore, the abbreviated electron configuration of sodium is [Ne]$3s^1$ (the electron configuration of neon is $1s^22s^22p^6$, which can be abbreviated to [He]$2s^22p^6$).



Neon	$1s^22s^22p^6$	
Aluminum	$1s^22s^22p^63s^23p^1$	becomes [Ne]$3s^23p^1$
Argon	$1s^22s^22p^63s^23p^6$	
Calcium	$1s^22s^22p^63s^23p^64s^2$	becomes [Ar]$4s^2$

Electron Configurations are useful for:

- Determining the valency of an element.
- Predicting the properties of a group of elements (elements with similar electron configurations tend to exhibit similar properties).
- Interpreting atomic spectra.
- This notation for the distribution of electrons in the atomic orbitals of atoms came into practice shortly after the Bohr model of the atom was presented by Ernest Rutherford and Niels Bohr in the year 1913.

Writing Electron Configurations

Shells

The maximum number of electrons that can be accommodated in a shell is based on the principal quantum number (n). It is represented by the formula $2n^2$, where ‘n’ is the shell number. The shells, values of n, and the total number of electrons that can be accommodated are tabulated below.

Shell and ‘n’ value	Max. Electrons in the Electron Configuration
K shell, n=1	$2*1^2 = 2$
L shell, n=2	$2*2^2 = 8$
M shell, n=3	$2*3^2 = 18$
N shell, n=4	$2*4^2 = 32$

Subshells

The subshells into which electrons are distributed are based on the Azimuthal quantum number (denoted by ‘l’).

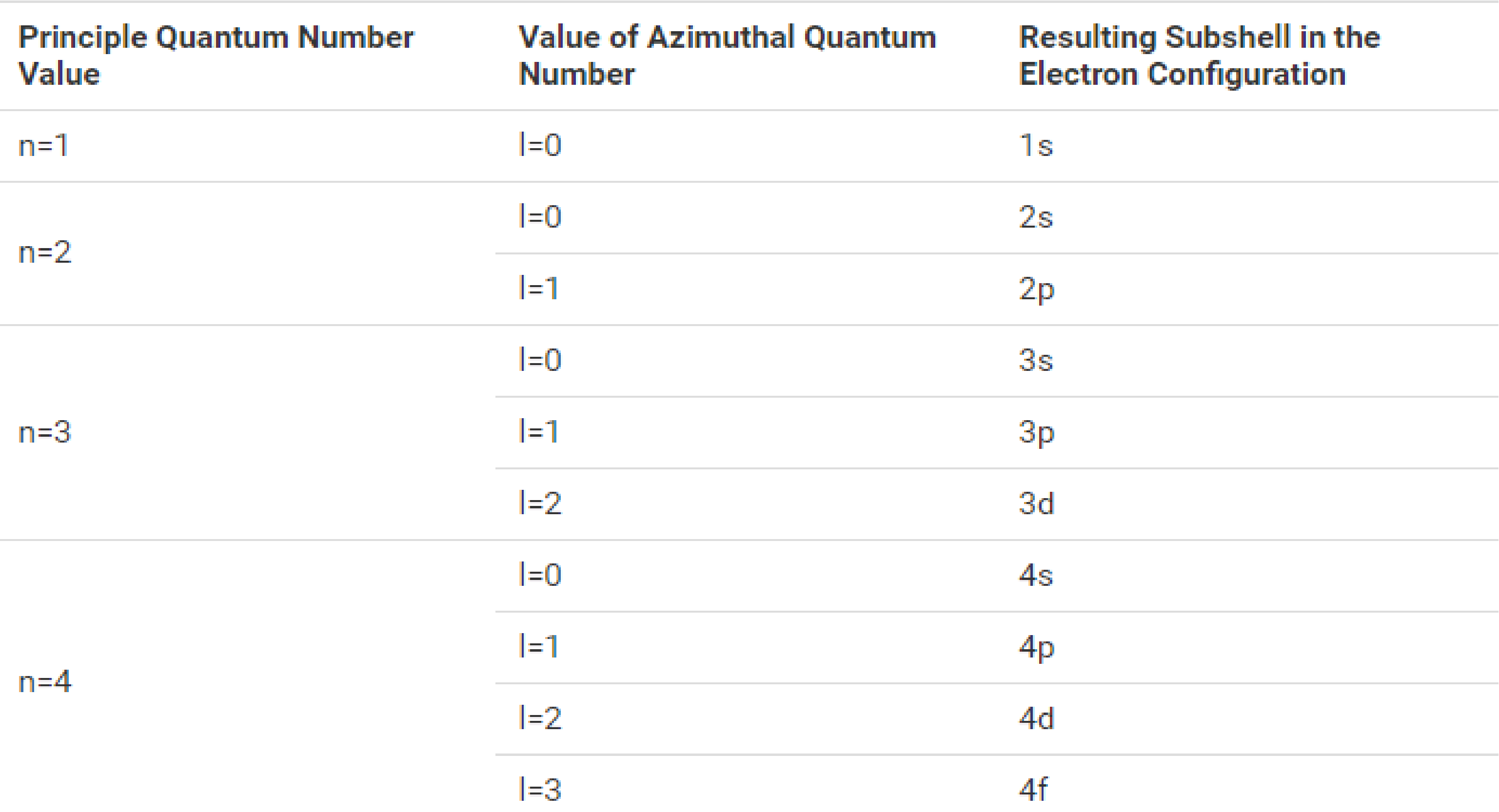
This quantum number is dependent on the value of the principal quantum number, n. Therefore, when n has a value of 4, four different subshells are possible.

When n=4. the subshells correspond to l=0, l=1, l=2, and l=3 and are named the s, p, d, and f subshells respectively.

The maximum number of electrons that can be accommodated by a subshell is given by the formula 2*(2l + 1).

Therefore, the s, p, d, and f subshells can accommodate a maximum of 2, 6, 10, and 14 electrons respectively.

All the possible subshells for values of n up to 4 are tabulated below.



Principle Quantum Number Value	Value of Azimuthal Quantum Number	Resulting Subshell in the Electron Configuration
n=1	l=0	1s
n=2	l=0	2s
	l=1	2p
n=3	l=0	3s
	l=1	3p
	l=2	3d
n=4	l=0	4s
	l=1	4p
	l=2	4d
	l=3	4f

Thus, it can be understood that the 1p, 2d, and 3f orbitals do not exist because the value of the azimuthal quantum number is always less than that of the principal quantum number.

Notation

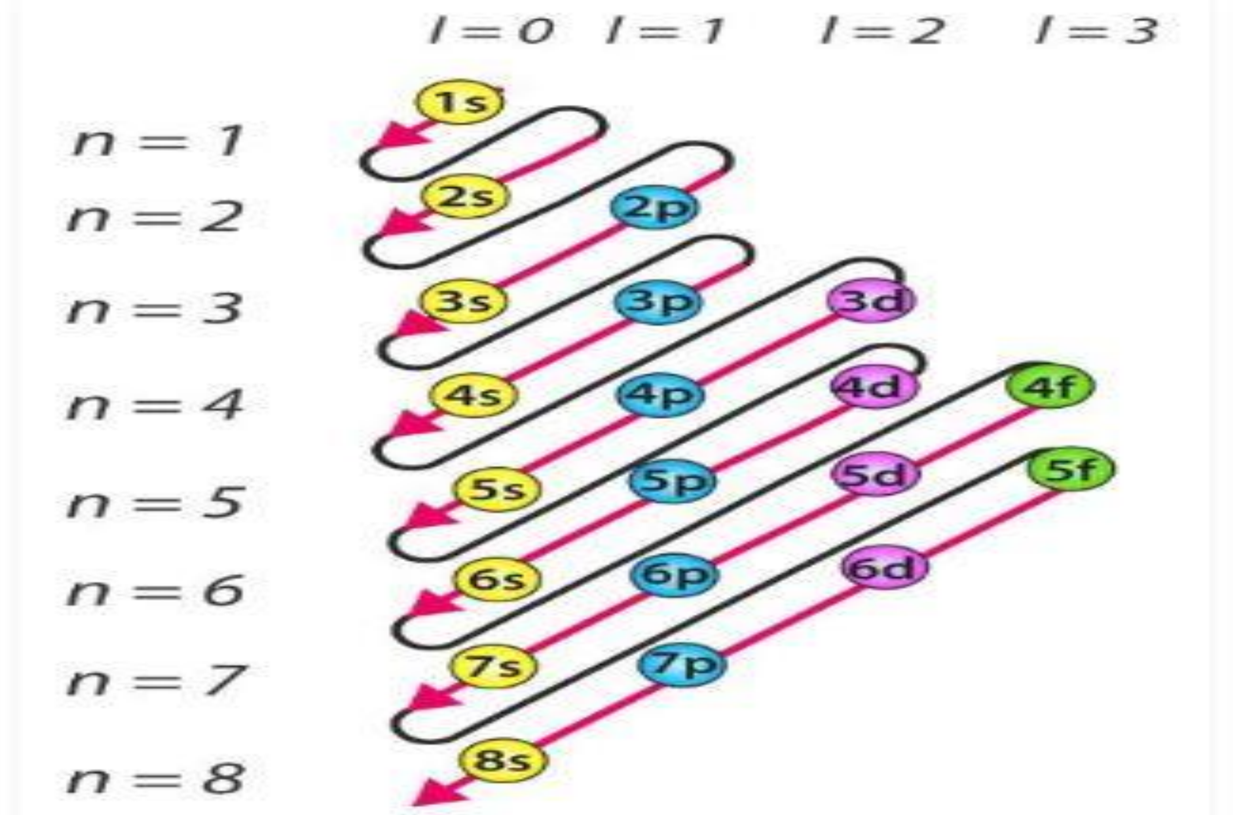
- The electron configuration of an atom is written with the help of subshell labels.
- These labels contain the shell number (given by the principal quantum number), the subshell name (given by the azimuthal quantum number), and the total number of electrons in the subshell in superscript.
- For example, if two electrons are filled in the ‘s’ subshell of the first shell, the resulting notation is ‘$1s^2$’.
- With the help of these subshell labels, the electron configuration of magnesium (atomic number 12) can be written as $1s^2\ 2s^2\ 2p^6\ 3s^2$.

Filling of Atomic Orbitals

Aufbau Principle

- This principle is named after the German word ‘Aufbeen’ which means ‘build up’.
- The Aufbau principle dictates that electrons will occupy the orbitals having lower energies before occupying higher energy orbitals.
- The energy of an orbital is calculated by the sum of the principal and the azimuthal quantum numbers.
- The order in which the energy of orbitals increases can be determined with the help of the (n+l) rule, where the sum of the principal and azimuthal quantum numbers determines the energy level of the orbital.
- Lower (n+l) values correspond to lower orbital energies. If two orbitals share equal (n+l) values, the orbital with the lower n value is said to have lower energy associated with it.
- According to this principle, electrons are filled in the following order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p…

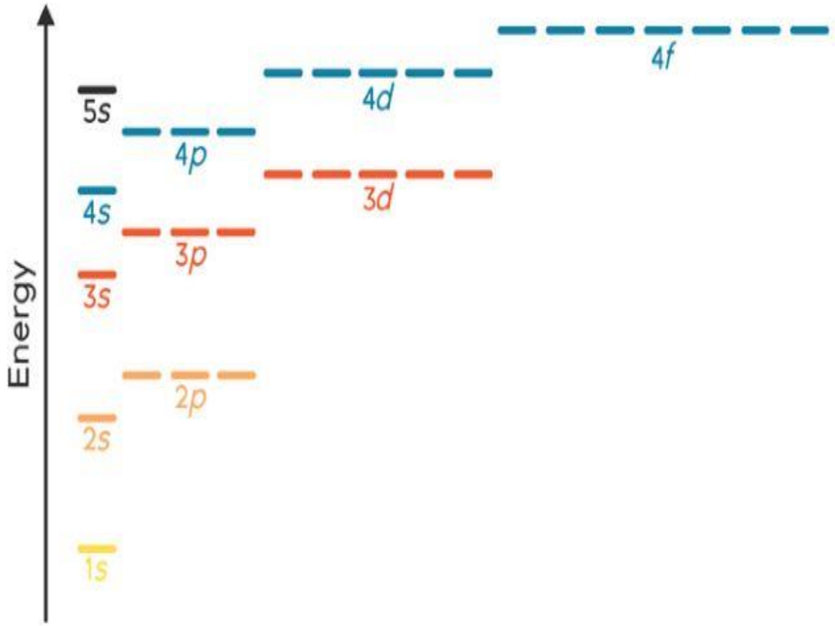
The order in which electrons are filled in atomic orbitals as per the Aufbau principle is illustrated below.



It is important to note that there exist many exceptions to the Aufbau principle such as chromium and copper. These exceptions can sometimes be explained by the stability provided by half-filled or completely filled subshells.

Exceptions

- The electronic configuration of chromium is [Ar]$3d^5 4s^1$ and not [Ar]$3d^4 4s^2$ (as suggested by the Aufbau principle). This exception is attributed to several factors such as the increased stability provided by half-filled subshells and the relatively low energy gap between the 3d and the 4s subshells.
- The energy gap between the different subshells is illustrated below.



Half filled subshells feature lower electron-electron repulsions in the orbitals, thereby increasing the stability. Similarly, completely filled subshells also increase the stability of the atom.

Therefore, the electron configurations of some atoms disobey the Aufbau principle (depending on the energy gap between the orbitals).

For example, copper is another exception to this principle with an electronic configuration corresponding to [Ar]$3d^{10} 4s^1$. This can be explained by the stability provided by a completely filled 3d subshell.

Electronic Configuration using the Aufbau Principle

Writing the Electron Configuration of Sulfur

- The atomic number of sulfur is 16, implying that it holds a total of 16 electrons.
- As per the Aufbau principle, two of these electrons are present in the 1s subshell, eight of them are present in the 2s and 2p subshell, and the remaining are distributed into the 3s and 3p subshells.
- Therefore, the electron configuration of sulfur can be written as **$1s^2 2s^2 2p^2 3s^2 3p^4$**.

Writing the Electron Configuration of Nitrogen

- The element nitrogen has 7 electrons (since its atomic number is 7).
- The electrons are filled into the 1s, 2s, and 2p orbitals.
- The electron configuration of nitrogen can be written as **$1s^2 2s^2 2p^3$**

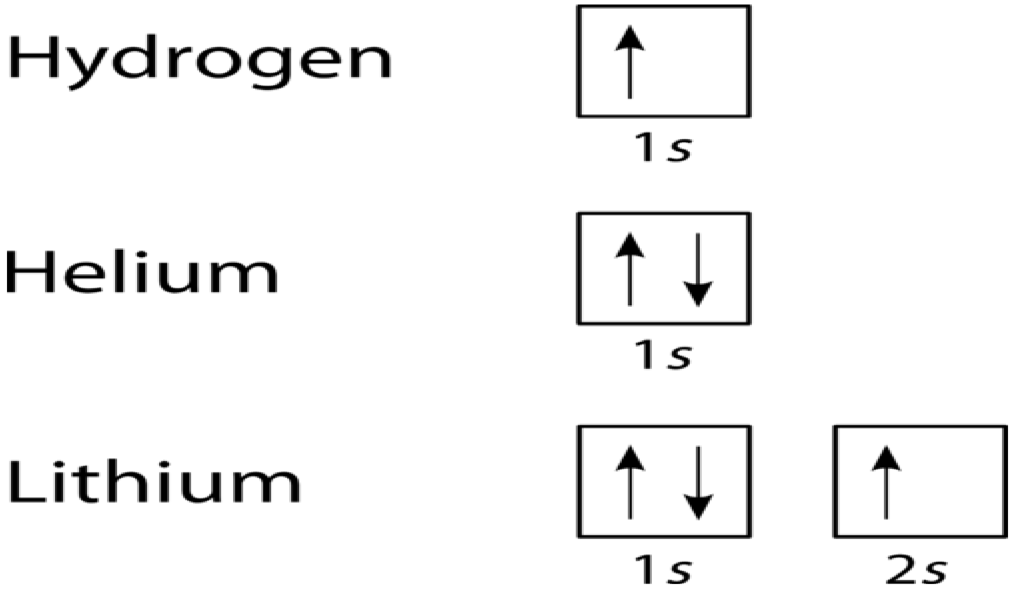
Pauli Exclusion Principle

- The Pauli exclusion principle states that a maximum of two electrons, each having opposite spins, can fit in an orbital.
- This principle can also be stated as “no two electrons in the same atom have the same values for all four quantum numbers”.
- Therefore, if the principal, azimuthal, and magnetic numbers are the same for two electrons, they must have opposite spins.

Pauli Exclusion Principle Example

- We can take a neutral helium atom as a common Pauli Exclusion Principle example. The atom has 2 bound electrons and they occupy the outermost shell with opposite spins. Here, we will find that the two electrons are in the 1s subshell where $n = 1$, $l = 0$, and $m_l = 0$.
- Their spin moments will also be different. One will be $m_s = -1/2$ and the other will be $+1/2$. If we draw a diagram then the subshell of the helium atom will be represented with 1 “up” electron and 1 “down” electron. In essence, 1s subshell will consist of two electrons, which have opposite spins.

Similarly, if we take Hydrogen it will have 1s subshell with 1 “up” electron ($1s_1$). Lithium will have the helium core (1s2) and then one more “up” electron ($2s_1$). What we are trying to depict here is that the electronic configurations of the orbitals is written in this manner.



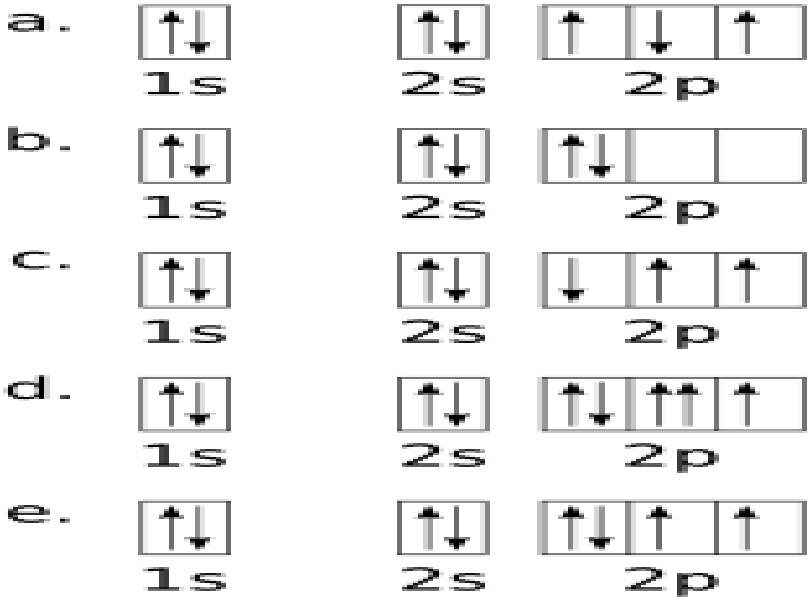
From the above example, we can further deduce that successive larger elements will have shells of successively higher energy. The number of electrons in the outer most shell is also directly related to the different chemical properties that elements possess. Elements with the same number of electrons in the outermost shell will have similar properties.

Hund’s Rule

According to Hund’s rule:

Before the double occupation of any orbital, every orbital in the sub level is singly occupied.

For the maximization of total spin, all electrons in a single occupancy orbital have the same spin. An electron will not pair with another electron in a half-filled orbital as it has the ability to fill all its orbitals with similar energy. A large number of unpaired electrons are present in atoms which are at the ground state. If two electrons come in contact they would show the same behaviour as two magnets do. The electrons first try to get as far away from each other as possible before they have to pair up.



Hund's Rule of Maximum Multiplicity

Hund's Rule of Maximum Multiplicity rule states that for a given electron configuration, the term with maximum multiplicity falls lowest in energy. According to this rule electron pairing in p, d and f orbitals cannot occur until each orbital of a given subshell contains one electron each or is singly occupied.

State Hund's Rule

It states that:

1. In a sublevel, each orbital is singly occupied before it is doubly occupied.

2. The electrons present in singly occupied orbitals possess identical spin.

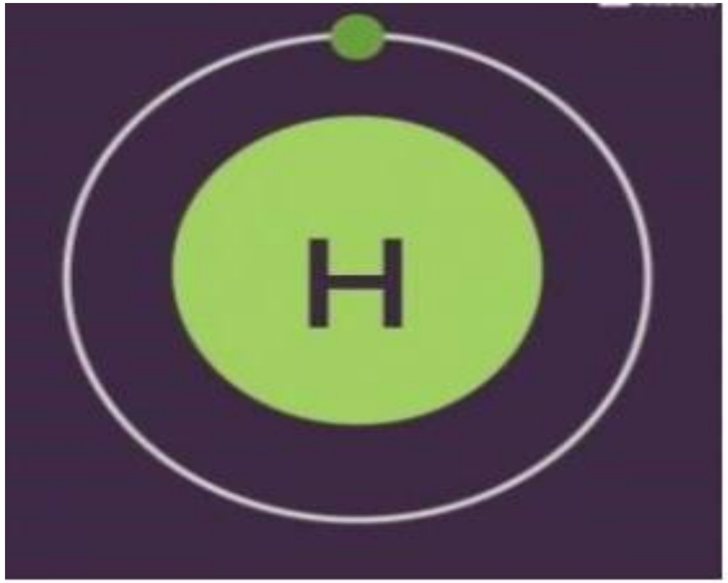
Explanation of Hund's Rule

- The electrons enter an empty orbital before pairing up. The electrons repel each other as they are negatively charged. The electrons do not share orbitals to reduce repulsion.
- When we consider the second rule, the spins of unpaired electrons in singly occupied orbitals are the same. The initial electrons spin in the sub-level decides what the spin of the other electrons would be. For instance, a carbon atom's electron configuration would be $1s^2 2s^2 2p^2$. The same orbital will be occupied by the two 2s electrons although different orbitals will be occupied by the two 2p electrons in reference to Hund's rule.

Examples

Electron Configuration of Hydrogen

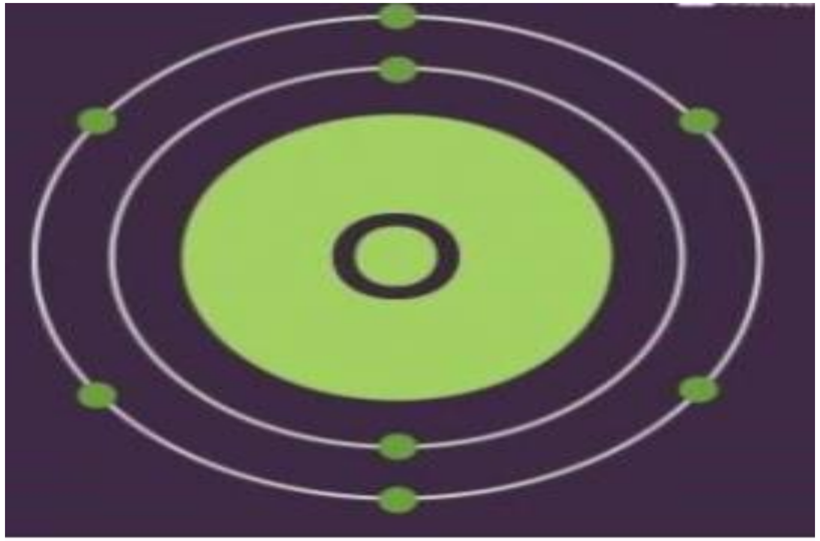
The atomic number of hydrogen is 1. Therefore, a hydrogen atom contains 1 electron, which will be placed in the s subshell of the first shell/orbit. The electron configuration of hydrogen is **$1s^1$**, as illustrated below.



Electron Configuration of Hydrogen

Electron Configuration of Oxygen

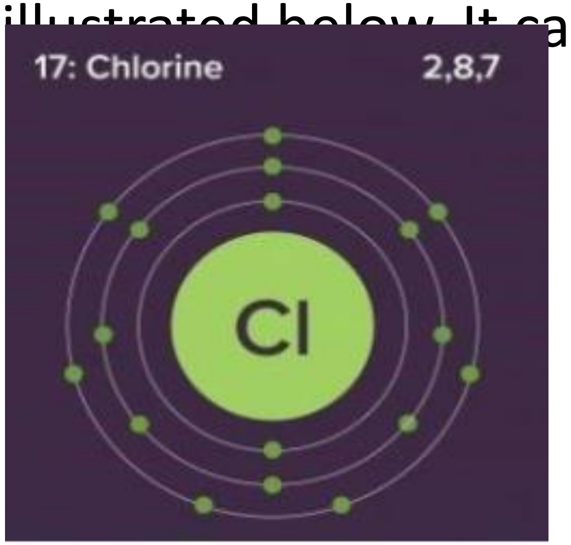
- The atomic number of oxygen is 8, implying that an oxygen atom holds 8 electrons. Its electrons are filled in the following order:
- K shell – 2 electrons
- L shell – 6 electrons
- Therefore, the electron configuration of oxygen is **$1s^2$ $2s^2$ $2p^4$**, as shown in the illustration provided below.



Electron Configuration of Oxygen

Chlorine Electronic Configuration

- Chlorine has an atomic number of 17. Therefore, its 17 electrons are distributed in the following manner:
- K shell – 2 electrons
- L shell – 8 electrons
- M shell – 7 electrons
- The electron configuration of chlorine is illustrated below. It can be written as $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^5}$ or as $[Ne]3s^2 3p^5$



Electron Configuration of Chlorine

Stability of Completely Filled and Half-filled Orbitals

Almost all the elements follow the same trend for writing electronic configuration. Sometimes when two sub-shells differ in the energies, an electron from the lower energy moves to higher energy.

This is because of two reasons:

- ***Symmetrical distribution:*** As everyone knows that symmetry leads to stability. The orbitals in which the sub-shell is exactly half-filled or completely filled are more stable because of the symmetrical distribution of electrons.
- ***Exchange energy:*** The electrons which are there in degenerate orbitals have a parallel spin and tend to exchange their position. Exchange energy is nothing but the energy released during this process. When the orbitals are half-filled or completely filled then the number of exchanges is maximum. Therefore, it’s stability is maximum.